I. Phenanthraquinoneimine Rearrangement-Structure and Novel Transformations of Phenanthraquinoneimide Anhydride

II. New Facets in the Utilization of Nucleophilic Systems Created With Trialkylphosphites

III. Reactions of 2, 3-Dibenzoylspiro (Cyclopropane-1, 9'-Fluorene) -A Reexamination

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

BY
CHANDRA SEKHAR PANDA

to the

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
1972

STATEMENT

I hereby declare that the research work embodied in this thesis "I. Phenanthraquinoneimine Rearrangement-Structure and Novel Transformations of Phenanthraquinone-imide Anhydride; II. New Facets in the Utilization of Nucleophilic Systems Created with Trialkylphosphites; III. Reactions of 2,3-Dibenzoylspiro(cyclopropane-1,9'-fluorene) - A Reexamination" is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology Kanpur, under the supervision of Professor S. Ranganathan.

The extent of information derived from the existing literature has been indicated in the body of the thesis at appropriate places, giving the source of information.

Chandra Sekhar Panda

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DEPARTMENT OF CHEMISTRY
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CERTIFICATE I

This is to certify that Mr. Chandra Sekhar Panda has satisfactorily completed all the courses required for the Ph.D. programme in Chemistry. These courses include:

Chm 500	Mathematics for Chemists
Chm 501	Advanced Organic Chemistry I
Chm 502	Advanced Organic Chemistry II
Chm 521	Chemical Binding
Chm 523	Chemical Thermodynamics
Chm 524	Modern Physical Methods in Chemistry
Chm 541	Advanced Inorganic Chemistry I
Chm 614	Organic Photochemistry
Chm 615	Electrocyclic Reactions
Chm 624	Valence Bond and Molecular Orbital Theory
Chm 800	General Seminar
Chm 801	Graduate Seminar
Chm 900	Graduate Research

Mr. Chandra Sekhar Panda has successfully completed his Ph.D. Qualifying Examination in October, 1968.

P.S. Goel

(P.S. Goel)
Head,
Department of Chemistry

D. Devaprabhakara

(D. Devaprabhakara)
Convener
Departmental Post-
Graduate Committee

CERTIFICATE II

Certified that the work contained in this thesis, entitled: "I. Phenanthraquinoneimine Rearrangement-Structure and Novel Transformations of Phenanthraquinoneimide Anhydride; II. New Facets in the Utilization of Nucleophilic Systems Created with Trialkylphosphites; III. Reactions of 2,3-Dibenzoylspiro(cyclopropane-1,9'-fluorene) - A Reexamination" has been carried out by Mr. Chandra Sekhar Panda under my supervision and the same has not been submitted elsewhere for a degree.

S. Ranganathan
Thesis Supervisor

Kanpur:
June 1972

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I am very happy in acknowledging the help rendered by all my friends in the Department; particularly that of Dr. R. Vaidyanathaswamy, Mr. R.K. Poddar, Mr. R.K. Mohanty,

Mr. D.N. Nanda, Mr. R.C. Munjal and Mr. Ramesh Kumar is unforgettable. I am very much thankful to Mr. R.D. Singh for carrying out the typing work competently. Thanks are also due to Mr. J.N. Sharma and his associates of Glass Blowing shop, Mr. A.H. Siddiqui and Mr. A.C. Acharya of the Micro-analytical Laboratory and Professor T.M. Srinivasan and the staff of the low temperature laboratory. The assistance given by Mr. S.N.Misra and Mr. R.K. Yadava has been commendable.

The tremendous endurance, exhibited by my wife during my stay here as a student is worth remembering for ever and I sincerely thank her.

Finally my thanks are also due to my loving parents and affectionate father-in-law for their constant encouragement and assistance.

Chandra Sekhar Panda

Kanpur
June, 1972

PREFACE

The thesis dealing with reaction mechanisms and synthesis is divided into three chapters, I: Phenanthraquinoneimine Rearrangement-Structure and Novel Transformations of Phenanthraquinoneimide-Anhydride; II: New Facets in the Utilization of Nucleophilic systems Created with Trialkylphosphites; III: Reactions of 2,3-Dibenzoylspiro(cyclopropane-1,9'-fluorene)- A Reexamination. Each chapter is subdivided into six parts as Section A: Introduction, Section B: Background, Section C: Present work, Section D: Spectra, Section E: Experimental and Section F: References. An Appendix pertaining to the NMR spectra of spiro-cyclopropane-1,9'-fluorenes has been included.

I: PHENANTHRAQUINONEIMINE REARRANGEMENT—STRUCTURE AND NOVEL TRANSFORMATIONS OF PHENANTHRAQUINONEIMIDE ANHYDRIDE[3]

The structure of phenanthraquinineimide anhydride (PQIA), product arising from phenanthraquinoneimine on thermolysis, is shown to be 10H-dibenzo-(c,e)phenanthro-(9',10':4,5)-imidazo-(1,2-a)azepin-10-one. The earlier structures proposed for PQIA have been shown to be incorrect. PQIA has been transformed by sequence involving hydrolysis and decarboxylation to 2-biphenylyl phenanthrimidazole, whose structure was established by independent synthesis.

PQIA undergoes a novel photochemical change to give tetrabenzophenazine by sequence involving $\pi_{2a} + \pi_{2a}$ addition, dis-rotatory opening and oxygen loss. The present work reports

the synthesis of several model systems particularly those related to 3H-indazole and 3,4-dihydro pyridazine-4-ones.

II: NEW FACETS IN THE UTILIZATION OF NUCLEOPHILIC SYSTEMS CREATED WITH TRIALKYLPHOSPHITES[1]

In connection with possible routes to the novel system, α,β-unsaturated nitroso, the trialkylphosphite deoxygenation of nitro compounds have been examined. β-Nitrostyrene reacts with trimethylphosphite in a highly exothermic manner to give phenyl acetyl dimethylphosphonate oxime. Triethyl and triisopropylphosphites also give similar products. Possible routes to the related nitroso cyclopropanes have been examined employing 2-nitro-spiro(cyclopropane-1,9'-fluorene) and 2-nitro-3-phenyl-spiro(cyclopropane-1,9'-fluorene). Whilst the former on reaction with triisopropylphosphite gave cyanomethylene fluorene, the later yielded the dimeric hydrocarbon, 1,4-bisfluorenylidene-2,3-diphenylbutane. Structures of these novel transformation products have been established by analytical, synthetic and degradative procedures and their formation rationalized on basis of model studies.

Possible electrocyclic reactions of the pentadiene anion systems created from cross conjugated dienones and trialkyl phosphites have been investigated with the acyclic dibenzal acetone and the cyclic methandienone. Dibenzal acetone gave as the sole isolable product the unusual double Michael addition compound whose formation indicates the creation of the predicted pentadiene anion system. Remarkably the steroidal dienone with

triethylphosphite at 145-150° underwent mere dehydration unaffecting the dienone system.

Unlike cyclopentadienones where the cyclopentadienide system can be created with trialkylphosphites, diphenyl cyclopropenone on reaction with triisopropylphosphite at room temperature gave no evidence for the anti-aromatic $4e^-$ cyclopropene anion; instead isopropyl α-phenyl cinnamate was isolated as the exclusive product.

The course of trialkylphosphite reactions with other substrates such as 3-bromophthalide are presented.

III: REACTIONS OF 2,3-DIBENZOYLSPIRO(CYCLOPROPANE-1,9'-FLUORENE) — A REEXAMINATION[2]

The reported rather unique transformations leading to unknown products of system trans-2,3-dibenzoylspiro(cyclopropane-1,9'-fluorene) has now been reexamined.

trans-2,3-Dibenzoylspiro(cyclopropane-1,9'-fluorene) on treatment with methanolic potassium hydroxide followed by hydrogen chloride gives - contrary to earlier report - the rearranged product 2,5-diphenyl-3-(9'-methoxy-9'-fluorenyl)-furan, whose structure is established by degradation as well as by synthesis involving 2,5-diphenyl-3-(9'-fluorenyl)furan cation generated from 2,5-diphenyl-3-(9'-hydroxy-9'-fluorenyl)-furan which in turn was synthesized from 2,5-diphenyl furyl magnesium bromide and fluorenone.

1,2-Dibenzoyl(1-flurenylidine)ethane has now been identified as the product that was isolated in the previous work from trans-2,3-dibenzoylspiro(cyclopropane-1,9'-fluorene) and methanolic potassium hydroxide followed by hydrogen chloride and further the role of 1,2-dibenzoyl(1-fluorenylidine)ethane as an intermediate in the trans-2,3-dibenzoylspiro(cyclopropane-1,9'-fluorene) → 2,5-diphenyl-3-(9'-methoxy-9'-fluorenyl)-furan change has been established. Both trans-2,3-dibenzoylspiro(cyclopropane-1,9'-fluorene) and 1,2-dibenzoyl(1-fluorenylidine)ethane give the same 1,2-dibenzoyl-1-(9'-fluorenyl)ethane whilst 2,5-diphenyl-3-(9'-methoxy-9'-fluorenyl)-furan undergoes hydrogenolysis to give 2,5-diphenyl-3-(9'-fluorenyl)furan.

APPENDIX:

The NMR spectra of diversely substituted spirocyclopropane-1,9'-fluorenes have been examined and the most favoured conformations of the cyclopropane ring with reference to the remaining rigid part have been correlated employing Johnson-Bovey Tables and taking advantage of the unusually shielded fluorenyl-8-proton.

Publications

1. S. Ranganathan and C.S. Panda, Tetrahedron Letters, 3841 (1971).
2. S. Ranganathan, C.S. Panda, T. Page and H. Shechter, J. Org. Chem., 37, 1071 (1972).
3. C.S. Panda and S. Ranganathan, Abstract 0-42-70, Convention of Chemists, Madras, India (1970).

CONTENTS

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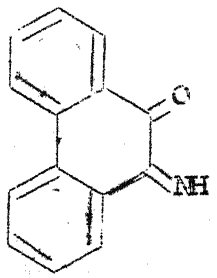
I. PHENANTHRAQUINONEIMINE REARRANGEMENT-STRUCTURE AND NOVEL TRANSFORMATIONS OF PHENANTHRAQUINONEIMIDE ANHYDRIDE

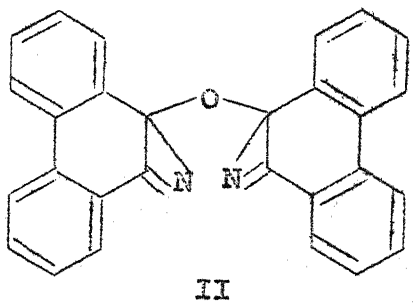
I.A INTRODUCTION

In the course of time no fewer than five structures have been proposed for the yellow compound obtained by Zincke in 1879 from phenanthraquinonemonoimine (I) on thermolysis and designated as phenanthraquinoneimideanhydride (PQIA), since the I $\longrightarrow$ PQIA change involves loss of elements of water.[1]

Zincke's attempts to determine the structure of PQIA were unsuccessful. This work was further taken up in 1893 by Graebe[2] who assigned the rather unusual structure II for PQIA. Subsequently in 1914 the molecular weight was determined by Oehme[3] who proposed structure III and IV for PQIA.



I



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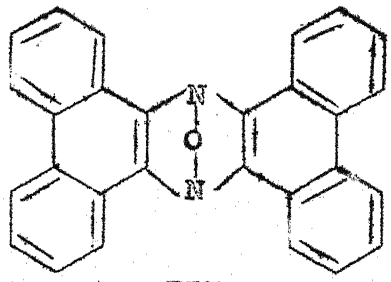
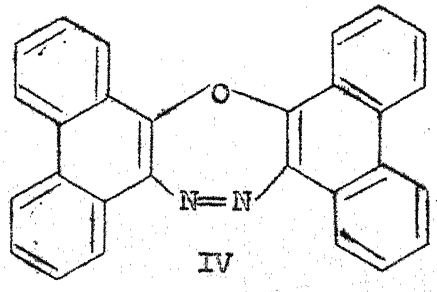
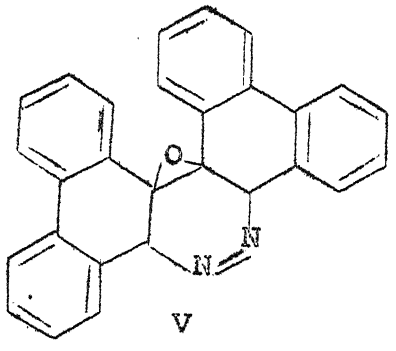


III

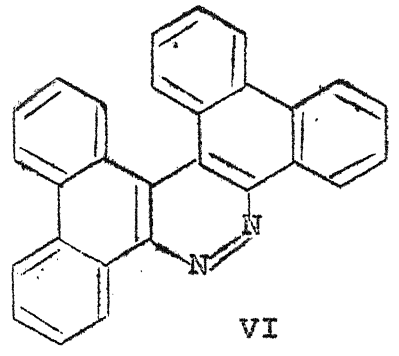


IV

A detailed study undertaken by Schonberg and Resenthal[4] in 1921 led to the epoxide structure V for PQIA. However, structure V, had to be abandoned in view of the findings by Hughes and Prankprakma[5] in 1966 that the anhydride possessed a carbonyl function. These authors confirmed the reported[4] transformation of PQIA to the pyridazine VI on thermolysis.

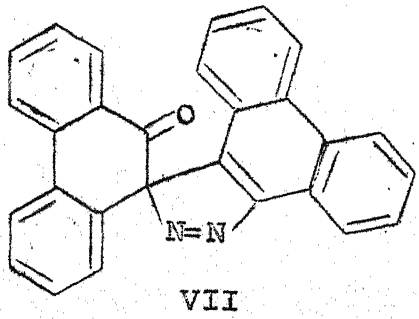


V

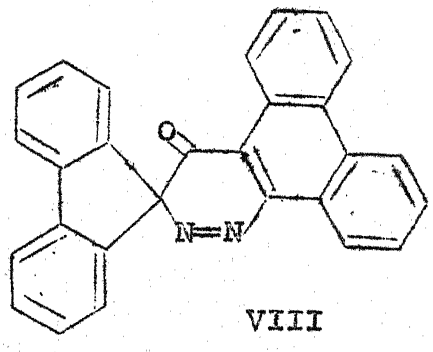


VI

Infact VI obtained from PQIA was compared by means of IR, picrate and mixed melting point with sample prepared from 10,10'-dinitro-9,9'-biphenanthryl and was found to be completely identical. On basis of this and information gathered from the mass spectral fragmentation, PQIA was considered to possess either structure VII or VIII with preference for VIII. Further, these authors excluded all the other structures in which the two nitrogen atoms are not proximate on basis of the PQIA ⟶ pyridazine change:



VII



VIII

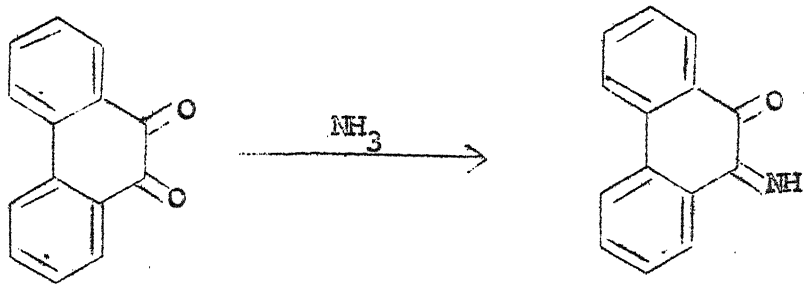
The proposed structures VII and VIII possessing scarce heterocyclic systems must be considered unusual because of the thermal stability implied in these. Our own interest in this area arose from a close examination of the conclusions of Hughes and Prankprakma.[5] We discerned many novel patterns in the I ⟶ PQIA ⟶ VI change.

The primary objective of our work was to establish the nature of PQIA to further understand the behaviour of this unique substance. It was also considered worthwhile to prepare models related to VII and VIII.

Much of the activity and the resulting uncertainity relating to the I ⟶ PQIA change is because of the rather unique nature of phenanthraquinonemonoimine (I). Whilst p-quinoneimines and their derivatives have been extensively studied, o-quinoneimines are scarce and phenanthraquinoneimine is perhaps the only known example of a stable o-quinonemonoimine. Consequently it would be proper to provide a background relating to the transformation of 1,2-diketones initiated by amine functions and proceeding through the corresponding monoimine intermediates.

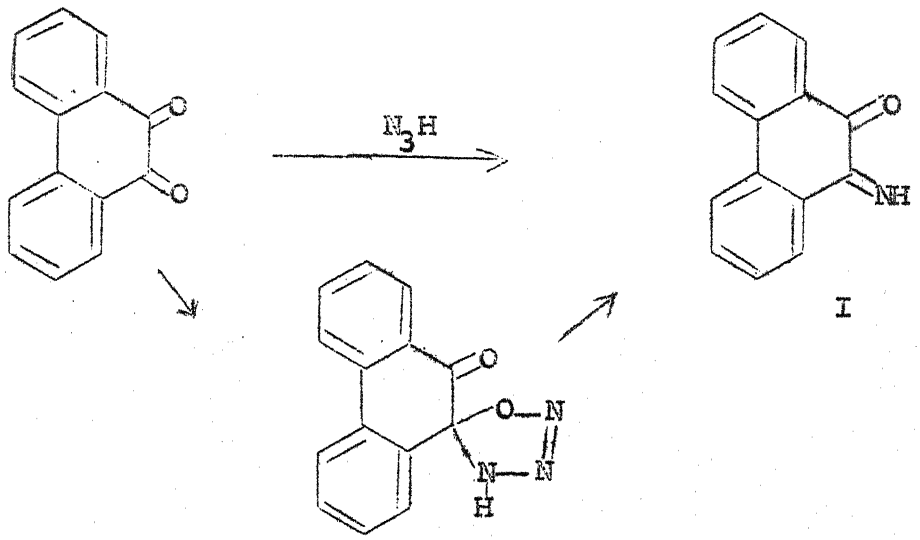
I.B. BACKGROUND

Interestingly phenanthraquinonemonoimine appears to be the only case of a stable 1,2-diketone monoimine. This compound is best prepared by the reaction of phenanthraquinone with saturated ethanolic ammonia:[6]



I

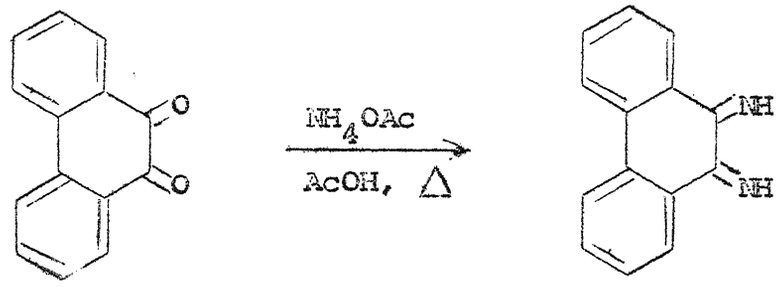
Compound I has also been reported[7] to arise from phenanthraquinone and hydrazoic acid, involving perhaps a cycloaddition-reversal pathway:



I

The unstable diimine[8] arise when phenanthraquinone is heated with

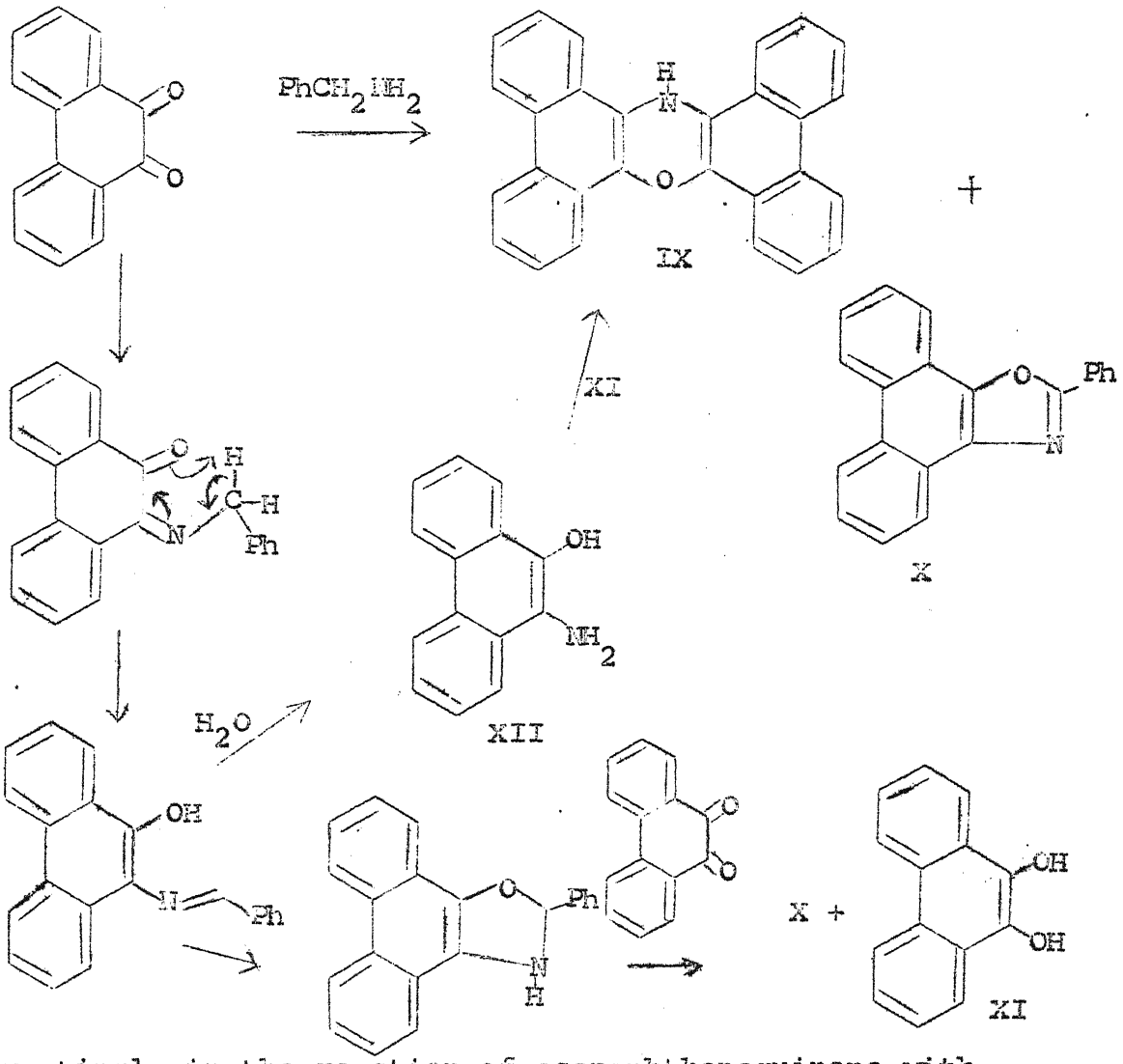
ammonium acetate in acetic acid:



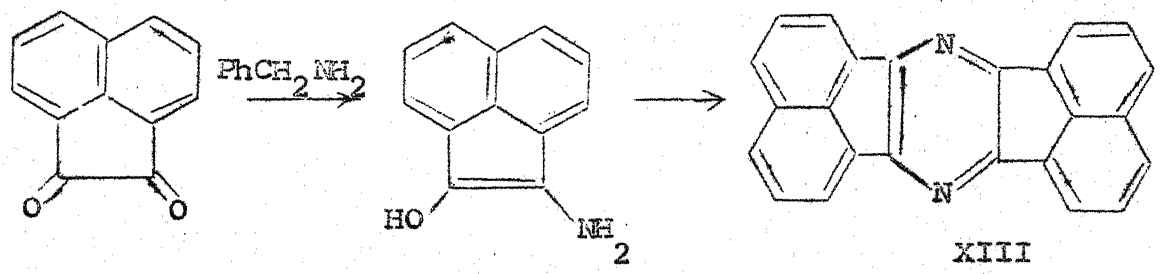
In general, 1,2-diketone-monoimines appear to be highly reactive compounds and this factor would account for the difficulties associated with the preparation of other members of this class. Although many transformations of 1,2-diketones have been brought about in presence of amines, no critical evaluation of this area has been made thus far. In this section an attempt is made to catalogue the properties of this elusive system. Only those cases where a 1,2-diketonemonoimine intermediate satisfactorily explains the transformations, are included.

Reactions Involving 1,2-Diketonemonoimine Intermediates

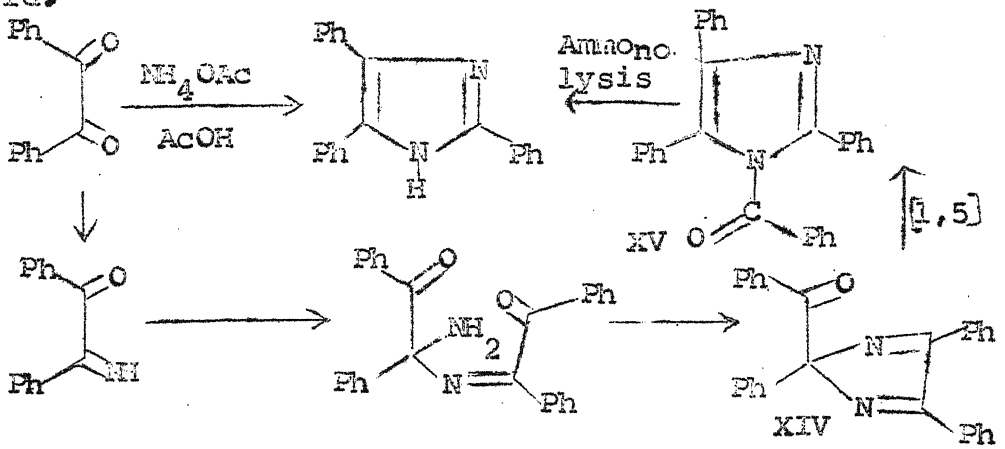
The substituted monoimines resulting from the reaction of either phenanthrenequinone or acenaphthenequinone undergo a variety of complex transformations that are initiated by a 1,5- shift of benzylic hydrogen. Phenanthrenequinone when treated with benzylamine gives IX and X:[9,10]



Interestingly in the reaction of acenaphthenequinone with benzylamine the intermediate related to XII undergoes dimerization to give acenaphthazine XIII:[11]

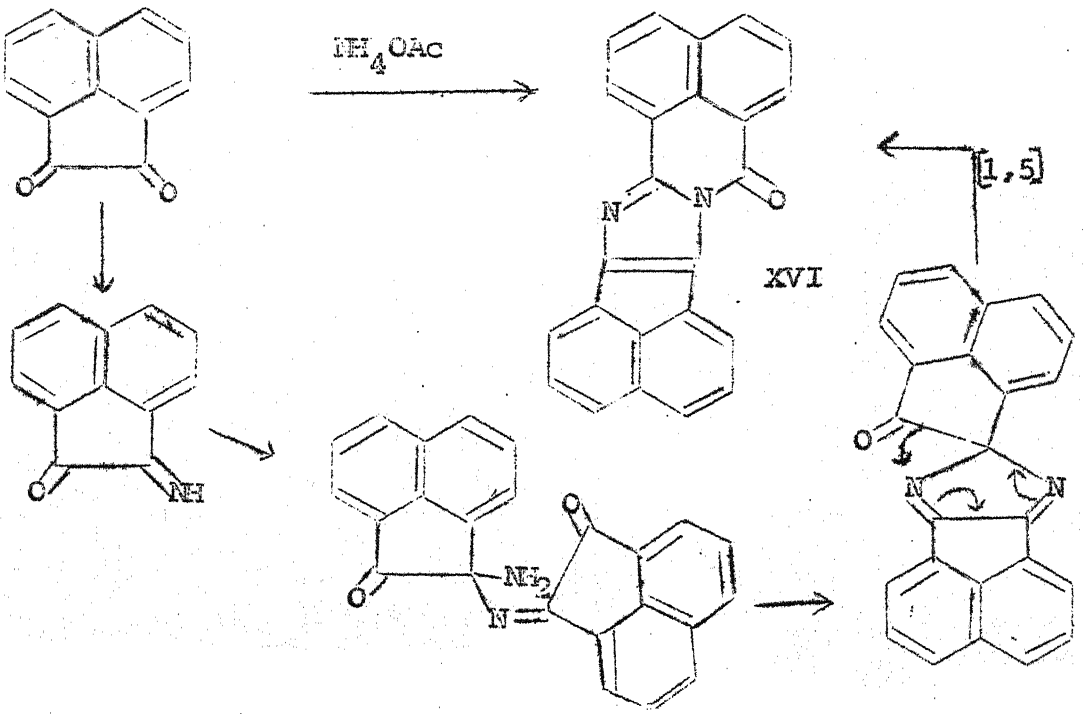


The most important reaction of 1,2-diketonemonoimines appears to be their transformation to imidazoles involving dimerization, dehydration and 1,5- shift.[12] These are exemplified in the classical transformation of benzil to lophine-2,4,5-triphenyl-imidazole- on heating in ammonium acetate and glacial acetic acid:[13]

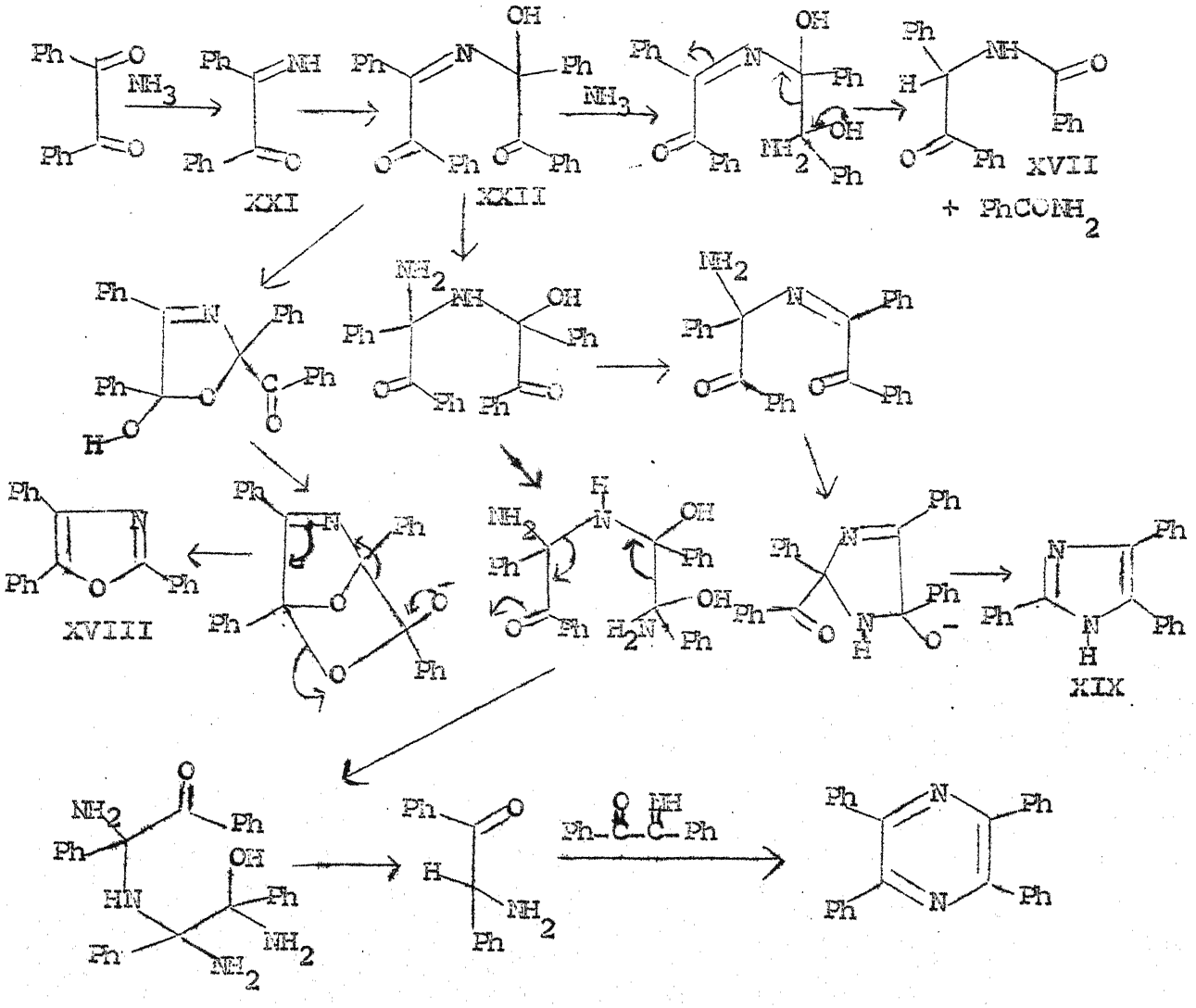


In accordance with this mechanism XIV undergoes ready rearrangement to XV.

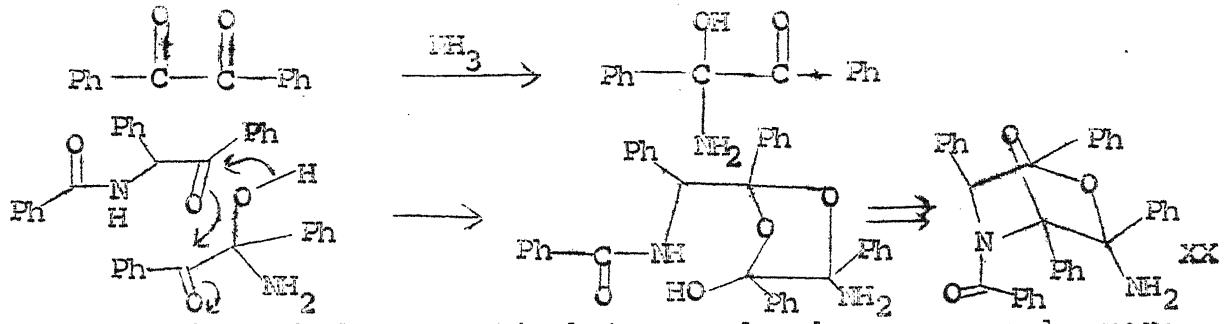
Similarly acenaphthenequinone with ammonium acetate is readily transformed to the imidazole XVI.[8]



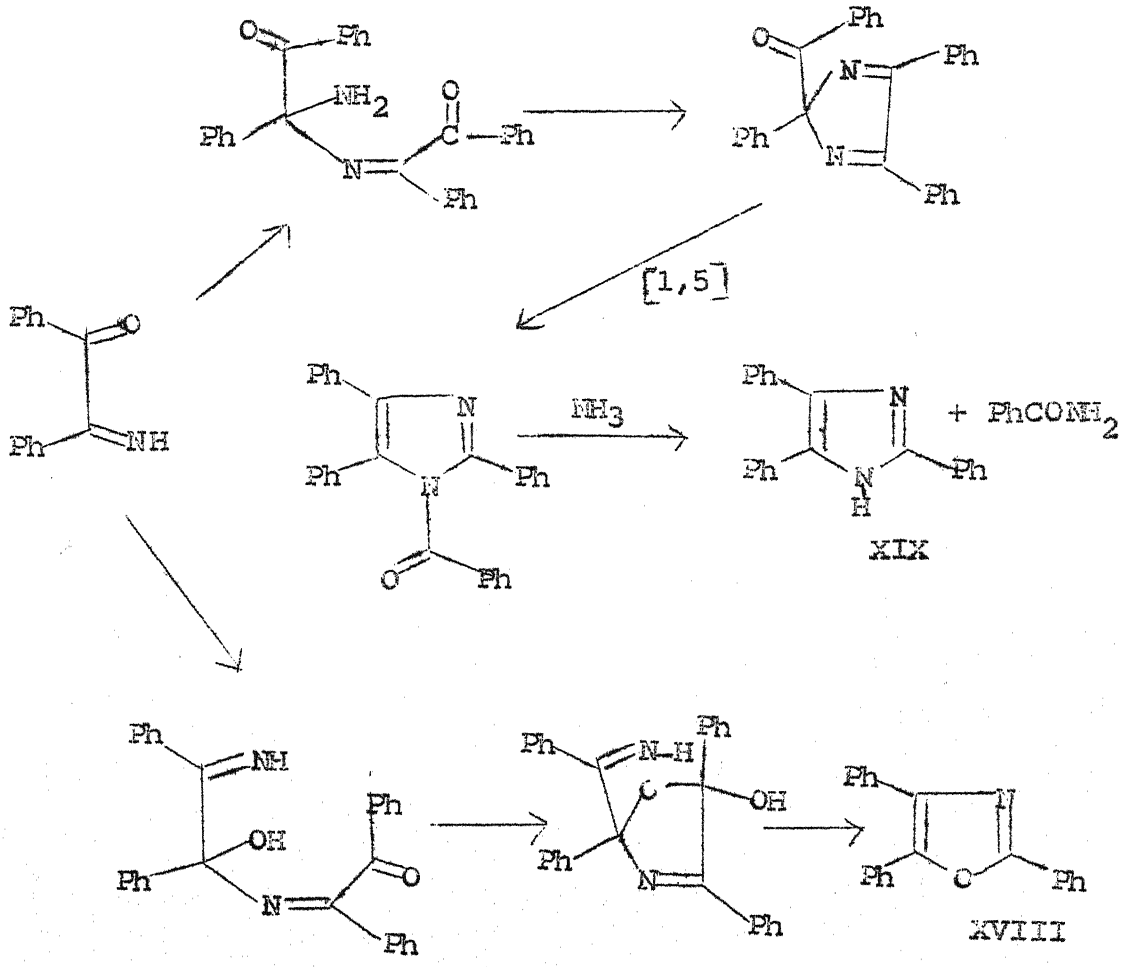
The much studied and apparently trivial transformation of benzil with ammonia correctly illustrates complexities that arise from intermediates having many reaction sites. The latest in this series[14] accounts the formation of ammonium benzoate, ethyl benzoate, N-desylamide (XVII), triphenyl-oxazole (XVIII) triphenylimidazole (XIX) and imabenzil (XX) on basis of an integrated mechanistic pathway. This approach envisages the initial formation of benzil monoimine (XXI) to give key intermediate (XXII).



The tentative structure (XX) for imabenzil has been proposed. The mechanism of its formation has also been speculated:

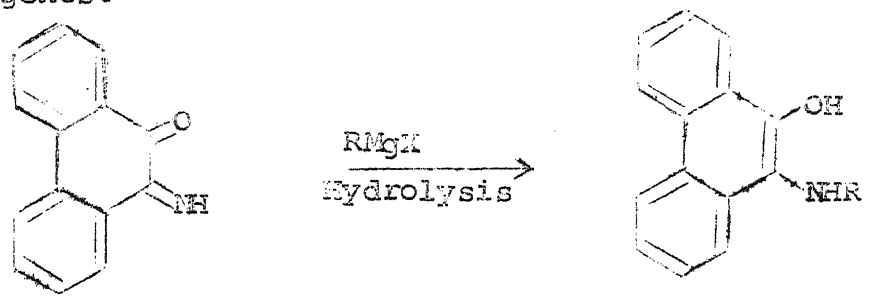


The formation of the aromatic heterocycles however can be more elegantly rationalized on basis of simple dimerization of benzilmonoimine:

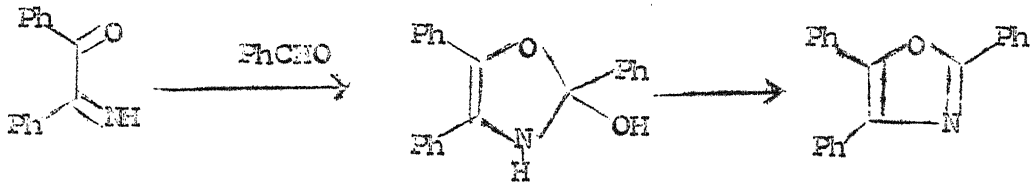


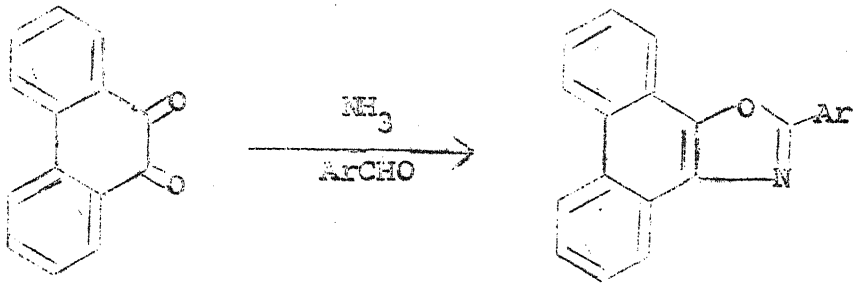
1,4-Addition with the formation of a N-C bond is possible

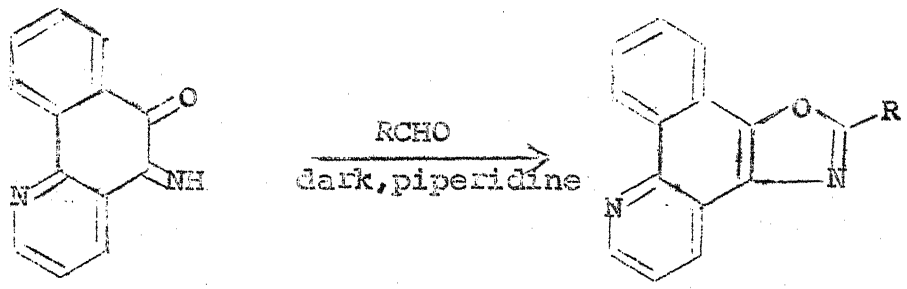
on reaction of phenanthraquinonemonoimine with Grignard reagents:[15]



1,2-Diketonemonoimines react with a variety of carbonyl compounds to give oxazoles:[16-18]

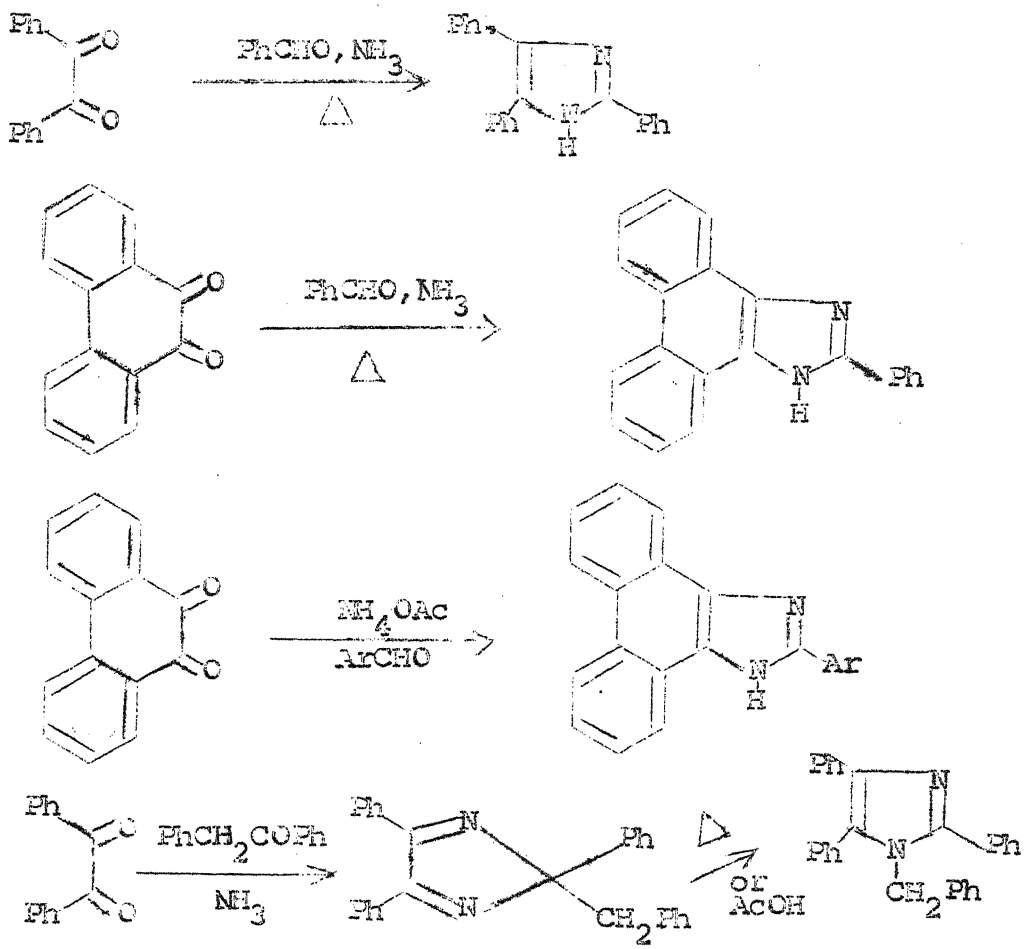




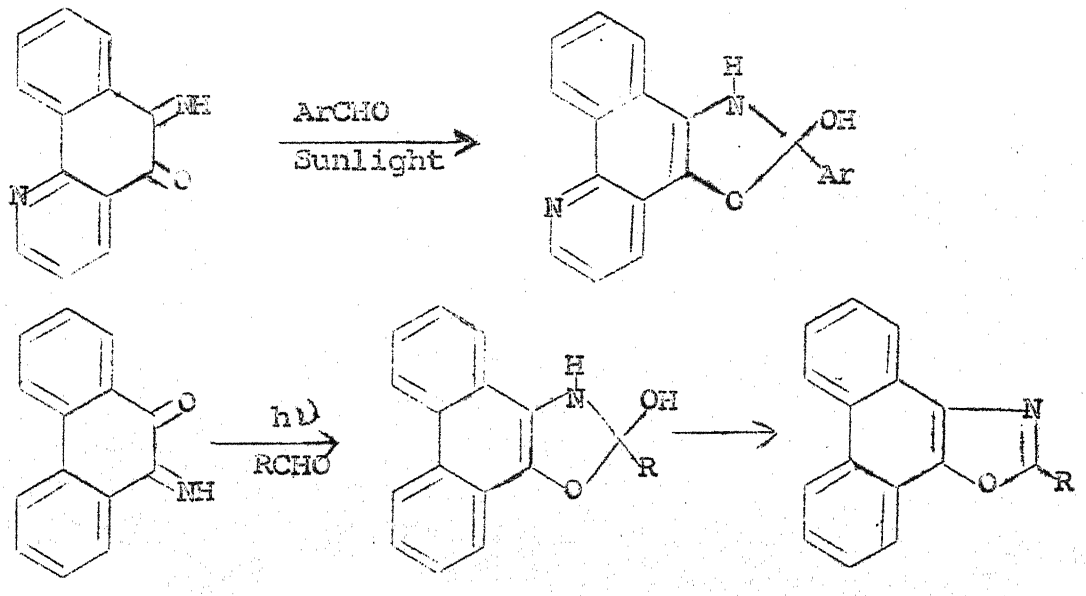


Under more drastic conditions the monoimines are transformed into diimines and further reaction of these species lead to imidazoles; infact this is a very general method for the

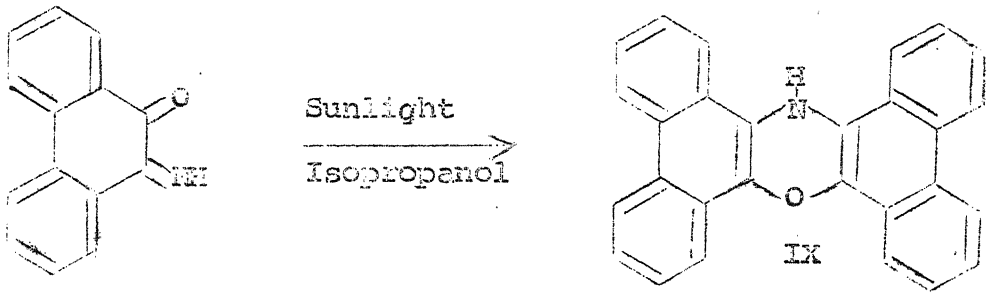
preparation of imidazoles:[19,20]



The addition of 1,2-diketonemonoimine to aldehydes has been also perfomned by photochemical methods:[18,21]

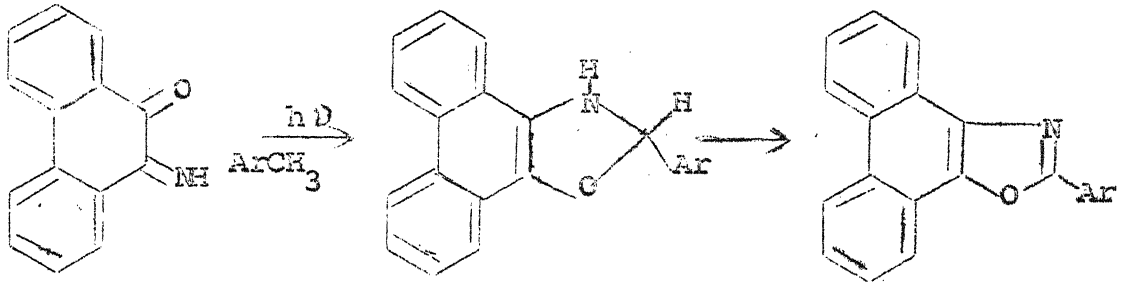


Phenanthraquinoneimine when photolysed in presence of isopropanol undergoes reduction and dimerization to give IX:[22]

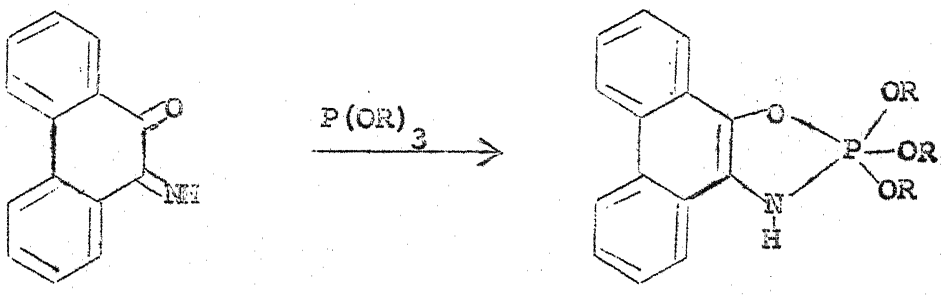


IX

Photolysis of phenanthraquinonemonoimine in presence of substituted toluenes undergo a remarkable change giving rise to the oxazoles,[23] necessarily involving extensive oxidation. It is believed that intermediates arising from homolytic scission of the aryl C-H bond are involved in this change:



Phenanthraquinonemonoimine undergoes an interesting (1+4) cycloaddition with trialkylphosphites.[24]



I.C. PRESENT WORK

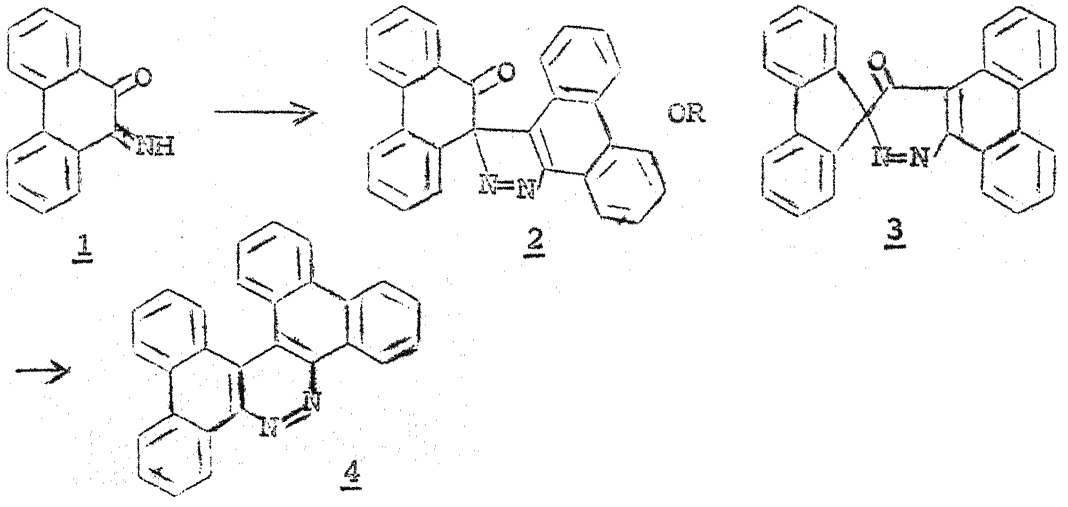
ABSTRACT

The structure of phenanthraquinoneimideanhydride (PQIA), product arising from phenanthraquinonemonoimine on thermolysis, is shown to be 10H-dibenzo(c,e)phenanthro(9',10':4,5)imidazo-(1,2-a)azepine-10-one. The earlier structures proposed for PQIA have been shown to be incorrect. PQIA has been transformed by sequence involving hydrolysis and decarboxylation to 2-biphenylyl phenanthrimidazole, whose structure was established by independent synthesis.

PQIA undergoes a novel photochemical change to give tetrabenzophenazine by sequence involving $\pi_{2a} + \pi_{2a}$ addition, disrotatory opening and oxygen loss. The present work reports the synthesis of several model systems particularly those relating to 3H-indazole and 3,4-dihydropyridazine-4-ones.

RESULTS AND DISCUSSION

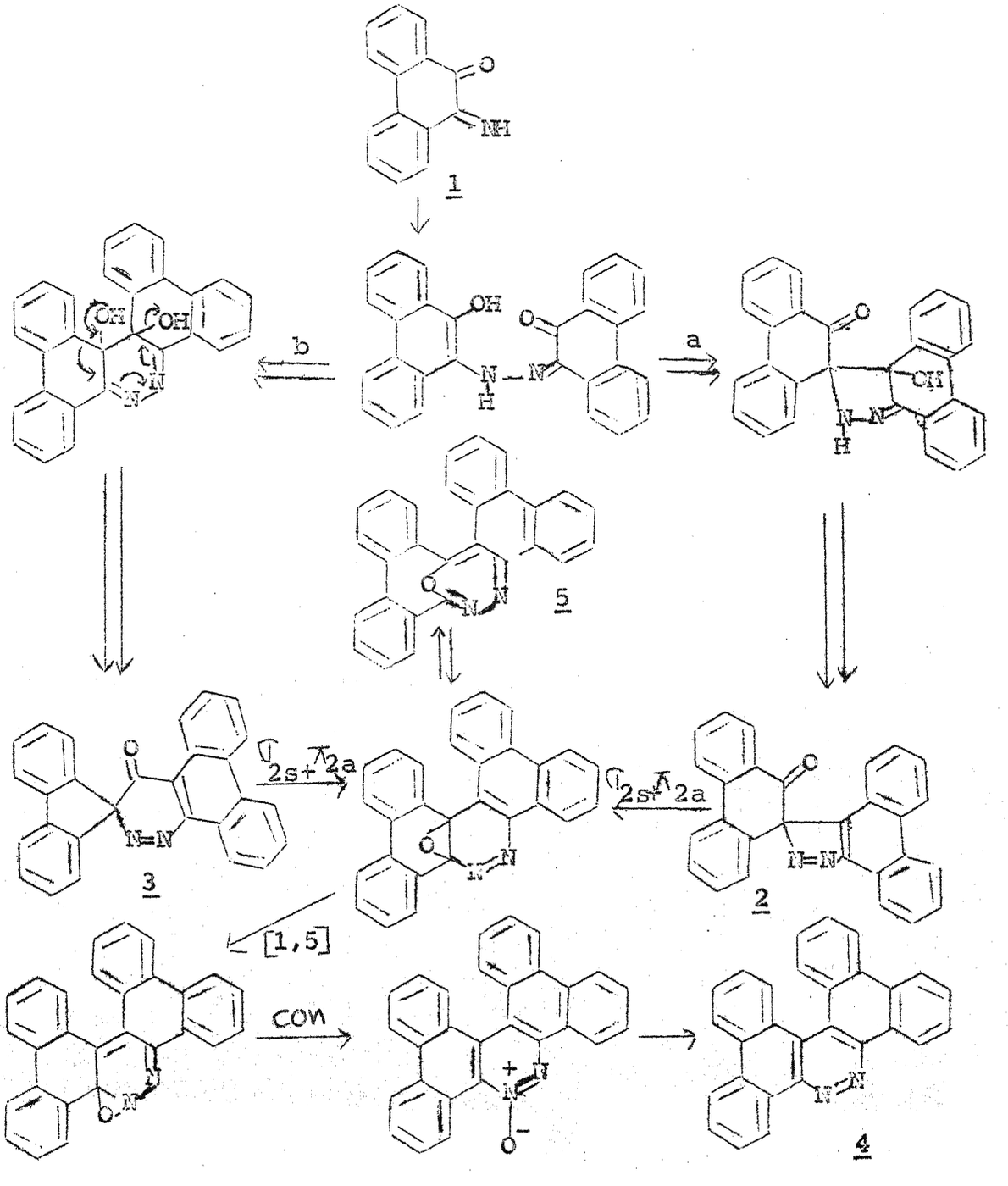
The genesis of the present work is related to the rationalization of the reported thermal transformation of phenanthraquinonemonoimine (1) to 2 or 3 and subsequently to cinnoline 4:



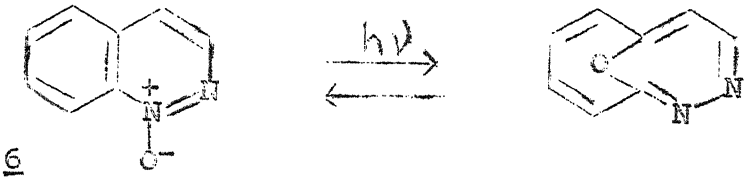
1 2 3 4

Diverse facets of molecular rearrangements can be discerned in the 1 → 4 change; further the formation of 2 or 3 involves the rather rare N–N bond formation in an addition process.

Several pathways for the 1 → 4 change could be considered and the one which embodies the essential features is presented below:



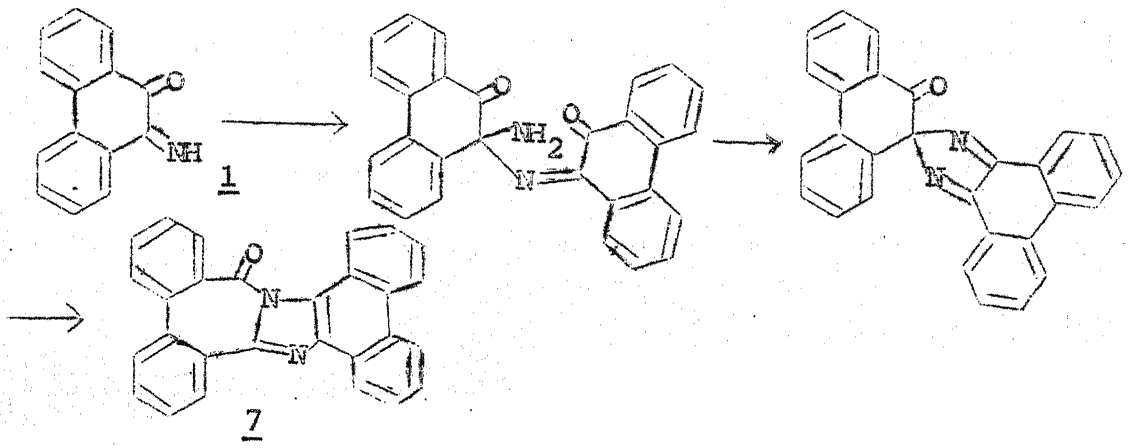
The first objectives in the present work was to conclusively establish the structures of compounds arising from 1. In the event the assignments to 2/3 and 4 were proved correct it was planned to examine facets of the proposed mechanistic pathways. Of particular interest was the possibility of creation of bridged annulenes by a novel photochemical route as exemplified[25] with 6:



6

Concurrently it was considered useful to explore novel routes to the rather scarce 3H-indazoles and 3,4-dihydropyridazine-4-ones present in 2 and 3 respectively.

Further characterization of the thermolysis product of PQIA appears to be warranted in view of the unexpected features implied in the 1 → 2/3 → 4 change. As elaborated in Section IB, 1,2-diketonemonoimines are transformed to imidazoles. This pathway is more logical since they occur by dimerization involving addition to the C=N moiety with the formation of a new C-N bond in contrast to situation that is required in the 1 → 2/3 change, namely, the formation of a N-N bond. Consequently phenanthraquinonemonoimine was expected to lead to imidazole 7 involving addition, dehydration and 1,5-shift:



7

Parenthetically, it has to be stated that unlike with 1,2-diketone monoimines, dimerisation of 1 involving N-N bond formation might be more facile because of the generation of the phenanthrene skeleton by such a process.

Phenanthraquinonemonoimine (1)* was prepared by the reaction of phenanthraquinone with saturated ethanolic ammonia.

---

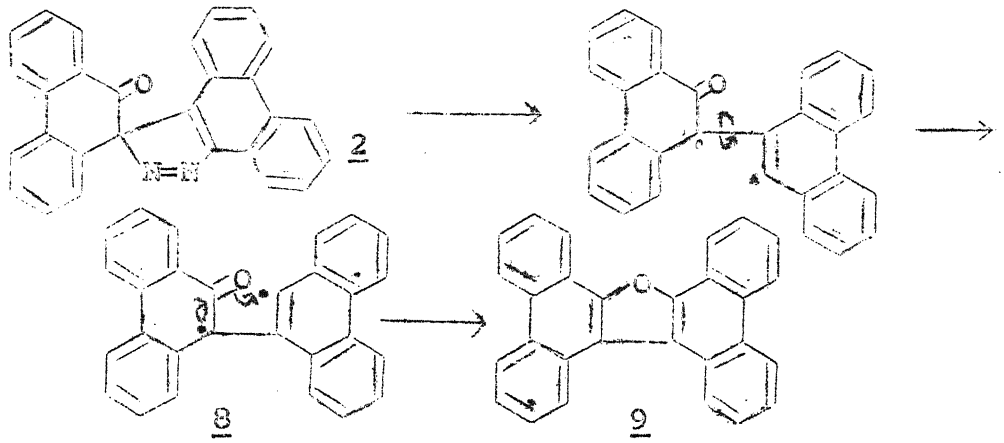
* mp. 158-159° (lit.[6] mp 159°).
IR: ν_{max} KBr (cm^{-1}): 1661, 1500, 1441 and 1275.
TLC: Single Spot R_f: 0.63 (Benzene:Ethyl acetate,50:50).

Phenanthraquinoneimideanhydride (PQIA)** was obtained either by treatment of 1 with acetic anhydride[1,5] in 27% yields or by a novel method involving reflux of o-dichlorobenzene solutions of 1 in 25% yields. The crude product was crystallized from pyridine and in all the present work crystalline samples were employed.

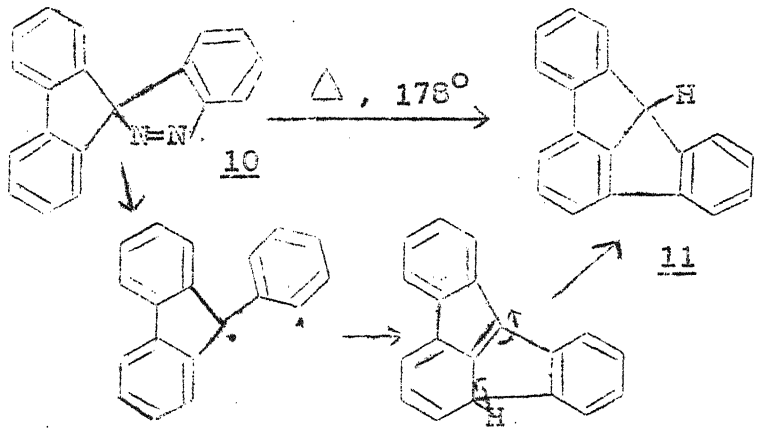
** mp. 260° (lit.[5] mp 257°).
IR: ν_{max} KBr(cm^{-1}): 1712, 1441, 1323 and 921.
TLC: Single spot R_f: 0.65 (Benzene:Ethyl acetate,50:50).

The absence of thermal nitrogen extrusion on basis of formulation 2/3 for PQIA was most perplexing and it was felt that such extrusion would help towards establishment of the structure of PQIA. Loss of nitrogen from 2 would give diradical

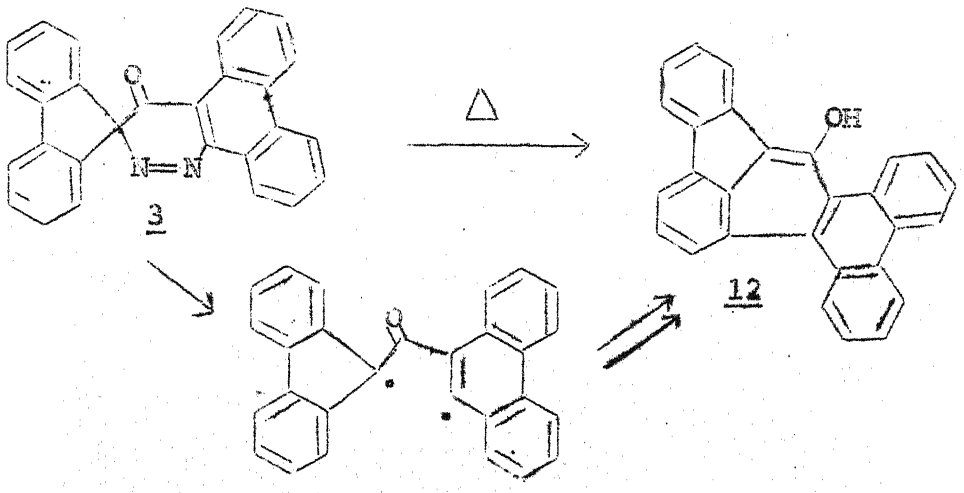
intermediate 8 which could cyclize to give the known furan 9:[26]



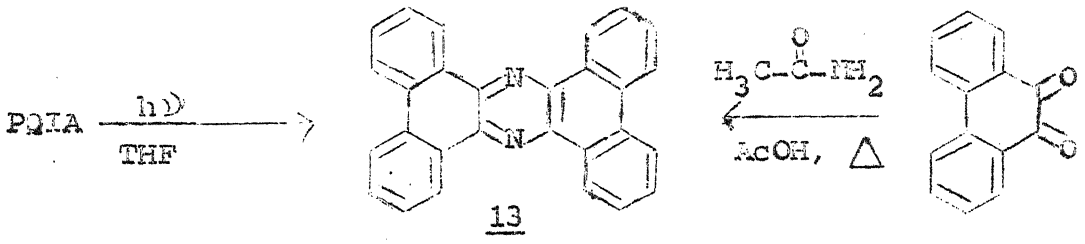
The possible consequences of nitrogen extrusion from structure 3 can be predicted on basis of the known[27] 10 ⟶ 11 change:



Compound 3 would then, be expected to yield 12:



In the event, photolysis of THF solution of pure PQIA using a 450 watt high pressure Hanovia lamp precipitated crystalline compound identified as tetrabenzophenazine 13 in 20% yields. The structural assignment for 13 is supported by analysis, IR* and by comparison with authentic sample prepared from phenanthraquinone and acetamide in a sealed tube:[28]



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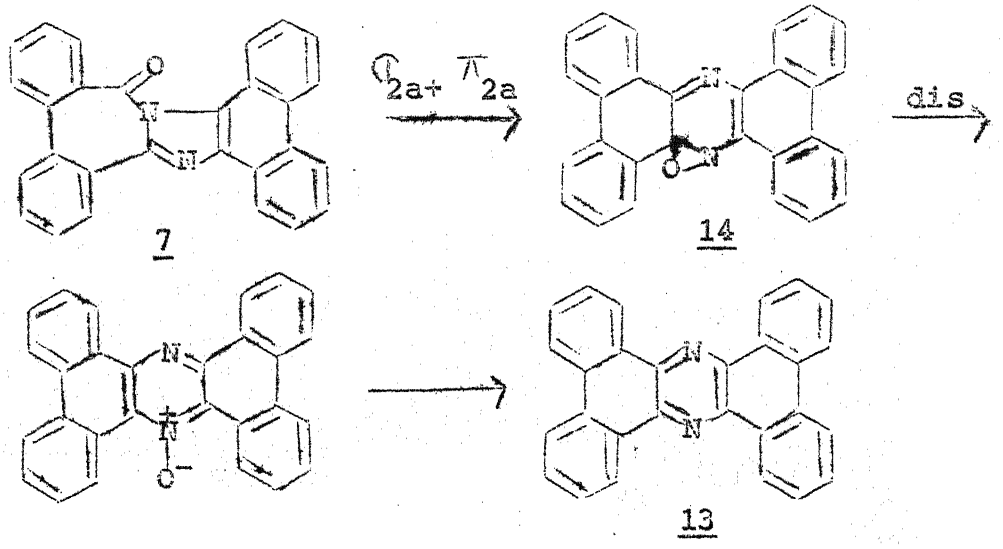
* mp. $>420^{\circ}$ (lit.[28] mp 440-441°).
IR: ν_{max} (KBr) (cm^{-1}): 1372, 1220, 755 and 720.

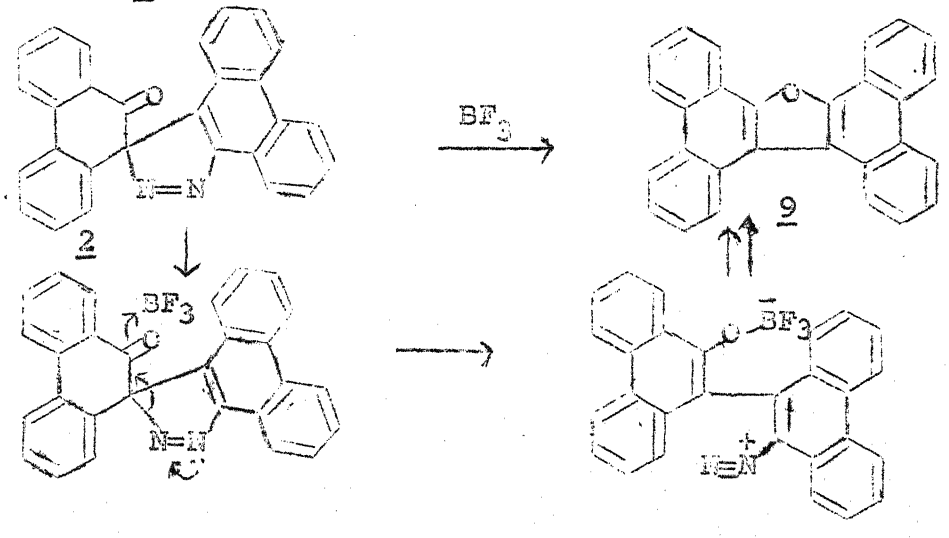
The rationalization of the PQIA → 13 change on basis of 2 and 3 would amount to a change of a 1,2-N=N-array to a 1,4 one and consequently would be one attended with elaborate bond gymnastics. This was the first indication that probably assignments 2 or 3 for PQIA are in error.



In contrast the formation of 13 from 7 can be explained readily on basis of a $\sigma_{2a} + \pi_{2a}$ change, dis-rotatary opening and oxygen loss (p.19).

Each of the proposed pathway in the 7 → 13 change is based on the known behaviour of the related intermediates. Many examples concerning the $\sigma_{2a} + \pi_{2a}$ change as well as the photochemical disrotatary opening can be found in "The Conservation of Orbital Symmetry".[29] The loss of oxygen from aromatic N-oxides have, in recent years, been frequently reported.[30] The 7 → 13 change is novel, fascinating and appears to be rather unique!

Having not achieved the nitrogen extrusion by thermal and photochemical means, attempts were made to effect the desired expulsion by using electrophiles, the expectations being exemplified with 2:



Treatment of a benzene solution of PQIA with BF_3, Et_2O instantaneously precipitated a white solid believed to be a salt on

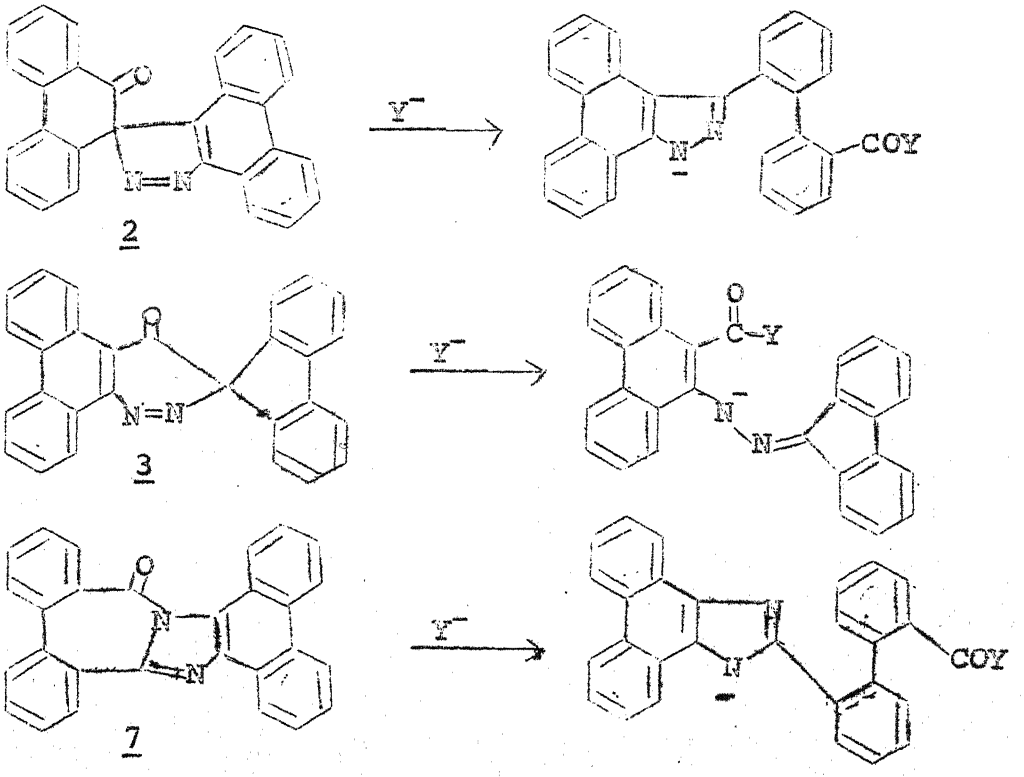
basis of IR.*

---

* IR : ν_{max} (KBr) (cm^{-1}): 1645, 1448, 1290, 1050 (broad) and 750.

The photochemical PMIA → 13 change strongly suggested that the nitrogens are not proximate and inspite of apparent favourable experimental evidence structures 2 and 3 became rather unlikely.

Experiments that would enable correlation of PMIA with either 2 or 3 or 7 were then designed. Examination of these structures reveals that each of these have an activated carbonyl grouping and consequently would be predicted to give derivatives of acids on treatment with nucleophiles:



This conclusion is in good agreement with the reported transformations of PQIA with a variety of nucleophiles[4] such as hydroxide, acetate and alcohols. The interesting aspect of these reactions are that it could be reversed with great ease, generally by thermal means, to PQIA. All these factors suggested the operation of a rather facile ring opening-ring closure process. It was then planned to use the ring opening reactions to give products that could be unambiguously synthesized.

The reaction of PQIA with methanolic potassium hydroxide gave as reported[4] an amorphous white solid which was identified as a carboxylic acid. The insolubility of this material in common solvents precluded further purification. Decarboxylation of this acid was effected in Cu/Quinoline to give crystalline material having the expected molecular formula $C_{27}H_{18}N_2$.*

---

* mp. 230°

IR : ν_{max} (KBr) (cm^{-1}) : 1610, 1455 and 1445.

MS : m/e 370.

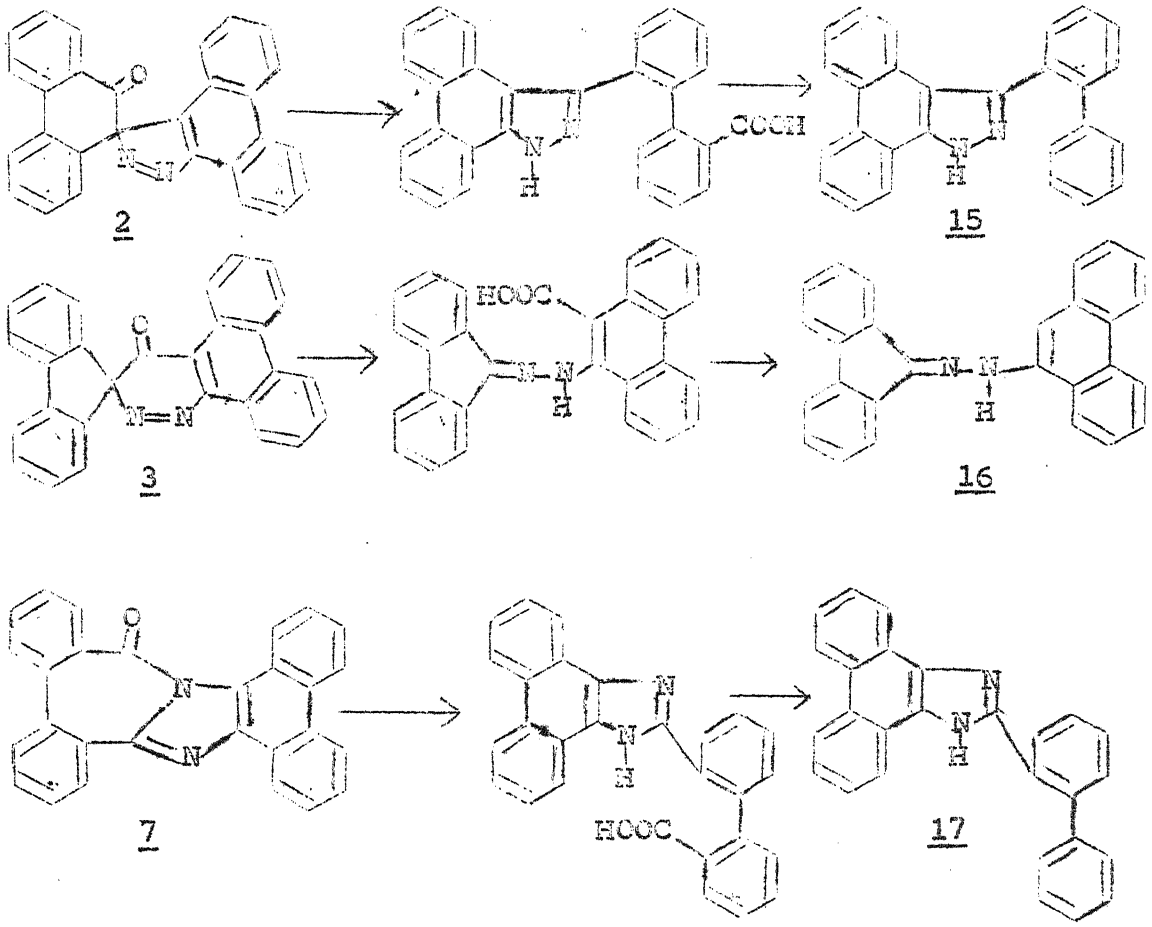
UV : λ_{max} (EtOH) (ϵ) : 357 (2716), 340 (2510), 303 (3045), 284 (18025), 257 (68307) and 229 (32256) nm.

UV : λ_{max} (EtOH, H^+) : 344 and 328 nm.

TLC: Single spot R_f: 0.80 (Methanol)

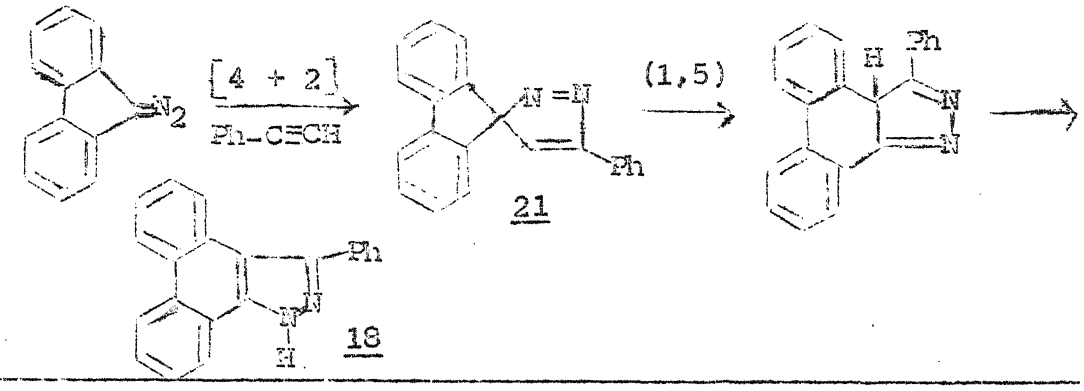
The hydrolysis-decarboxylation sequence when applied to the three possible candidates for PQIA, namely 2, 3 and 7, would give

respectively 15, 16 and 17, all having the observed molecular formula $C_{27}H_{10}N_2$:



In principle, the three possibilities namely 15, 16 and 17 could be synthesized in a straightforward manner thus providing a route for unambiguous identification of PQIA with either 2 or 3 or 7. Initially, however, it was considered profitable to effect the correlation of the decarboxylated product with proper models. With this aim models 18, 19 and 20 related to 15, 16 and 17 respectively were prepared.

Compound 18* was prepared[31] by the reaction of 9-diazofluorene with phenylacetylene. This reaction should be considered as taking place through a facile 1,5-shift of the initially formed adduct 21:



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* mp. 244-245° (lit.[31] mp 245-246°).

IR: ν_{max} (KBr) (cm^{-1}): 1400, 975.

UV: λ_{max} (EtOH) (ϵ): 340 (2100), 330s (1400), 323 (2100), 253 (34000) and 233s (26000) nm.

UV: λ_{max} ($EtOH,H^+$) : 339, 330 and 323 nm.

Models 19** and 20*** were prepared by standard procedures.[32,20]

** 19, mp. 148-150° (lit.[32] mp 151°).

IR: ν_{max} (KBr) (cm^{-1}): 1600, 1560, 1497 and 1255.

UV: λ_{max} (EtOH) (ϵ): 388 (35080) and 245 (72710) nm.

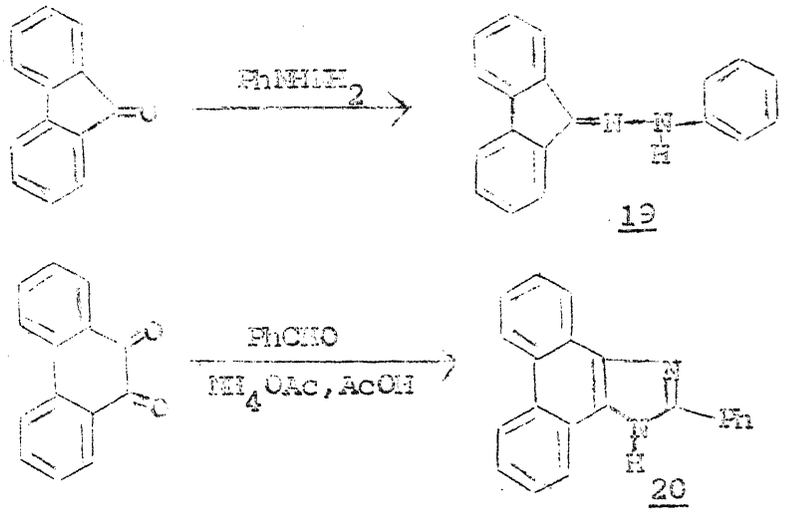
*** 20, mp. 312-314° (lit.[20] mp 314°).

IR: ν_{max} (KBr) (cm^{-1}): 1604 and 1450.

UV: λ_{max} (EtOH) (ϵ): 359 (8250), 344 (10900), 313 (19820) and 262 (59450) nm.

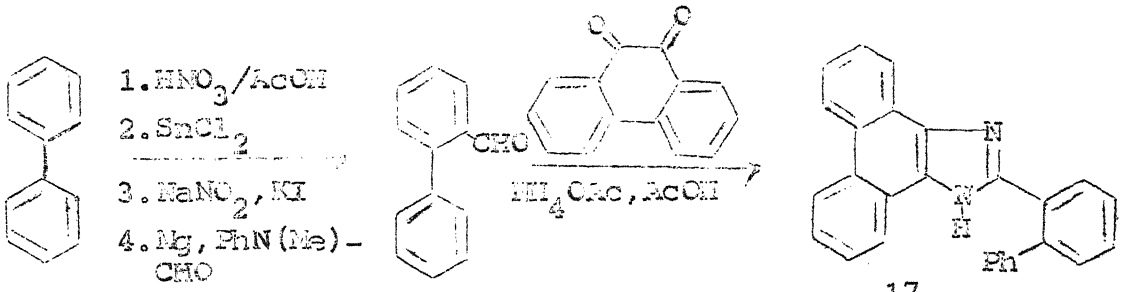
UV: λ_{max} ($EtOH,H^+$) : 349 and 335 nm.

TLC: Single spot R_f: 0.80 (Methanol)



The IR and UV comparisons completely ruled out the possibility that 19 was related to the decarboxylated product and consequently structure 3 for PQIA. Whilst IR comparisons could not conclusively favour either 18 or 20, as related to the decarboxylated product, the UV was in accord with 20 and consequently structure 7 for PQIA. Of particular importance was the large (>10 nm) hypsochromic shift observed in the UV with model 20 as well as the decarboxylated product on addition of acid. In contrast the UV spectrum of 18 was hardly affected by such treatment. Having obtained an indication that the decarboxylated product is infact the imidazole 17, its synthesis was carried out in an unambiguous manner. The key intermediate in the synthesis was 2-formyl biphenyl 21 which was prepared[33] from 2-iodobiphenyl by reaction of the corresponding Grignard reagent with N-methyl-formanilide.[33] The aldehyde 21 on treatment with phenanthrenequinone and ammonium acetate gave 17 in

excellent yields:



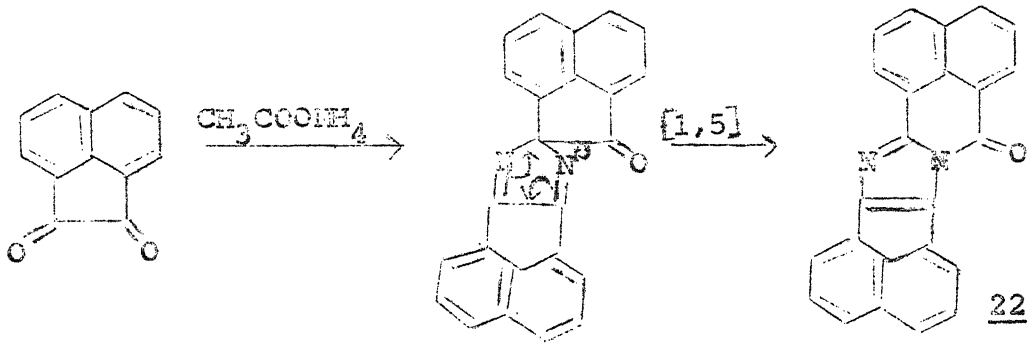
21 17

The sample that was obtained was identical in all respects to that of the decarbonylated product. PQIA must then have structure 7! This strongly suggested that the reported thermal correlation of PQIA with cinnoline 4 is in error. Whilst experiments were being planned to investigate the reported PQIA to cinnoline 4 change, a publication by Barton and Grinham[34] appeared in 1971 ≠ which clearly established that the reported PQIA → cinnoline change, as concluded in the present work ≠ was in error.

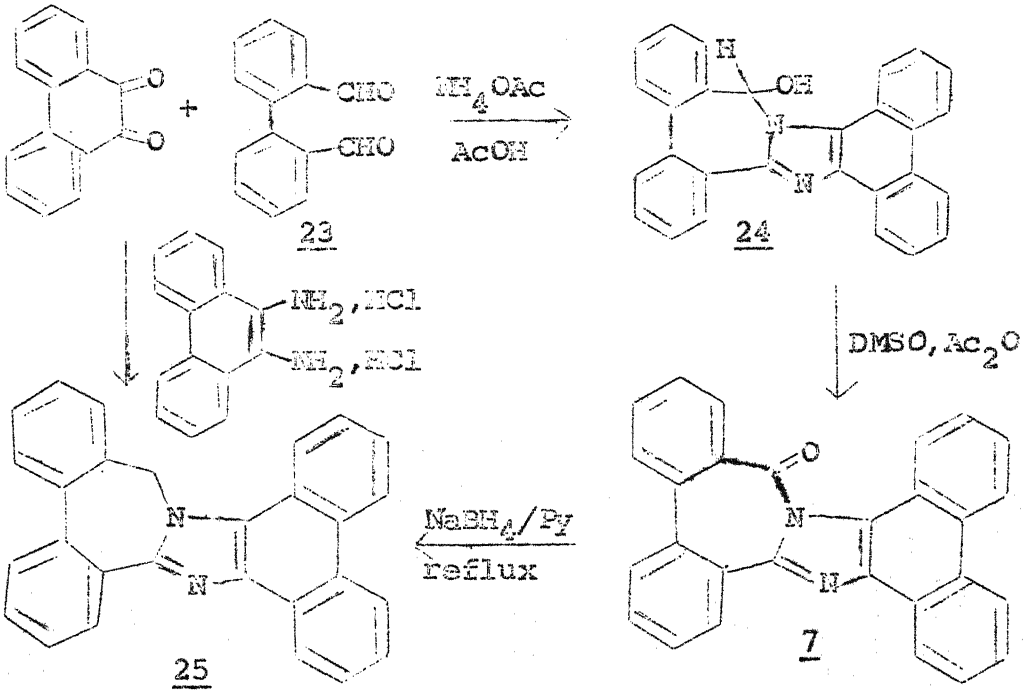
Interestingly these authors[34] apparently completely overlooked the 1966 work of Hughes and Prankprakma[5] published in Tetrahedron which as described in Section I-A led us to initiate this programme! Barton and Grinham, then, took up investigations relating to the nature of PQIA that was attempted previously[4] by Schonberg and Rosenthal in 1921 leading to structures having -N=N- for PQIA. In overlooking the 1966 work of PQIA these authors, unlike us, were not deflected from the logical pathway. Particularly the identification of the product resulting from acenaphthenequinone and ammonium acetate in 1970[8] as 22 made it

≠ Facets of this work were presented at the October 1970 Convention of Chemists held at Madras, India and well before this publication.

tempting to visualise the 1 ⟶ PQIA change by similar pathways resulting in structure 7:

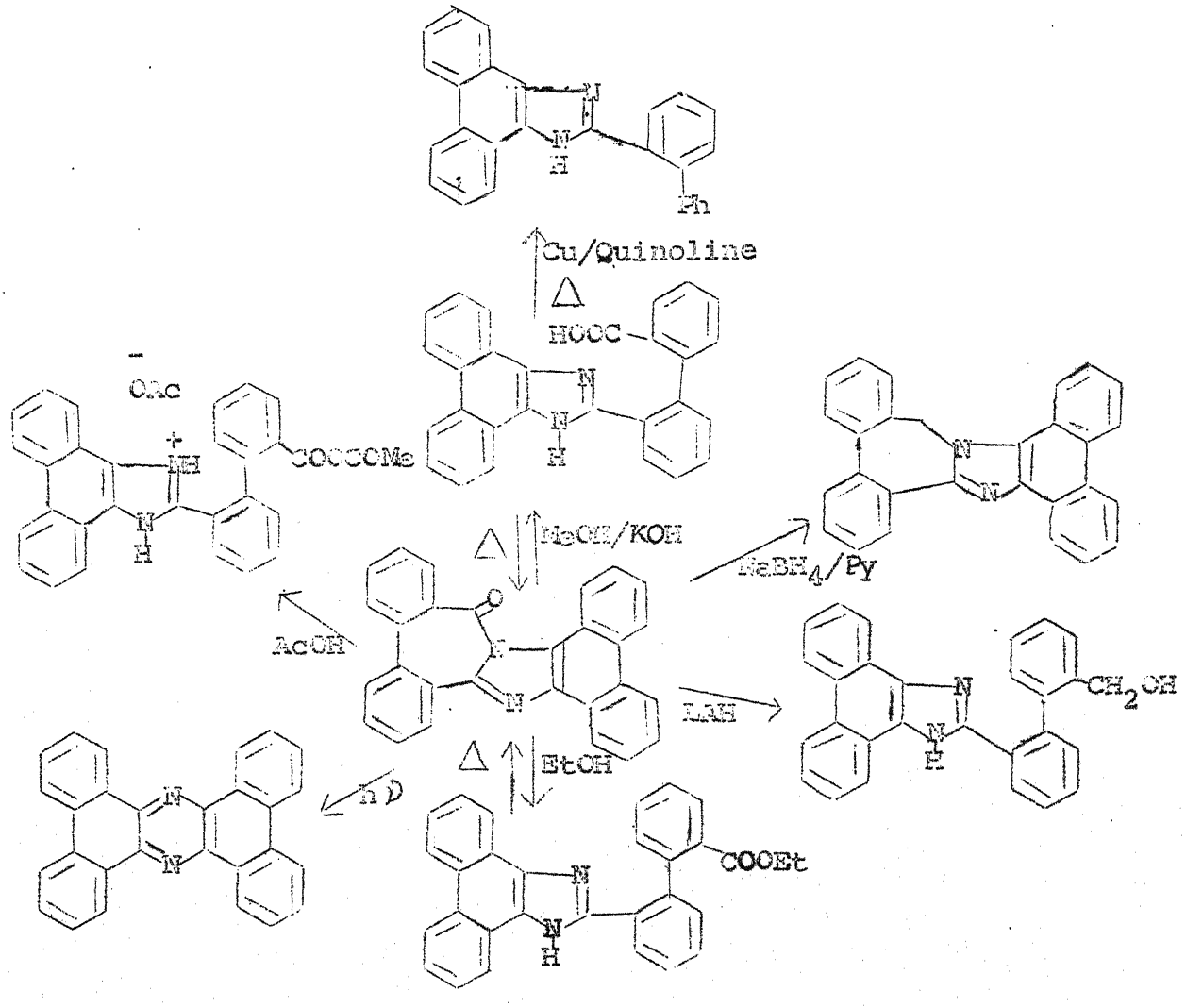


The identification of PQIA as 7 in the present work is in accordance with the conclusions reached by Barton and Grinham[34] and the essential features of their work are outlined below:



The condensation involving 23 and phenanthraquinone has no direct precedence and consequently the characterization of the product that was obtained in low yields as 24 is not unambiguous. Similar

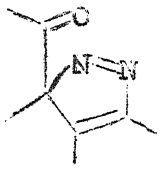
comment is also just for assignment of a structure for PQIA based on its transformation to 25 employing sodium borohydride in refluxing pyridine! Neverthless our own results, when taken with that of Barton and Grinham[34] leaves little doubt that PQIA has structure 7. It would be proper to explain all the reactions reported for this substance by several group of workers on basis of the structure arrived by us:



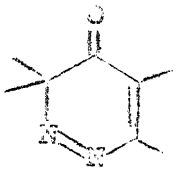
While efforts relating to the structural elucidation of PQIA were under way, parallel work aimed at the preparation of scarce

systems 26 and 27, which are part of the proposed structure 2 and 3 respectively for PQIA were also undertaken.

As mentioned earlier few examples of type 26 are known and 27 is a novel system. It was hoped that the behaviour of simpler substrates belonging to 26 and 27 will be easier to investigate.

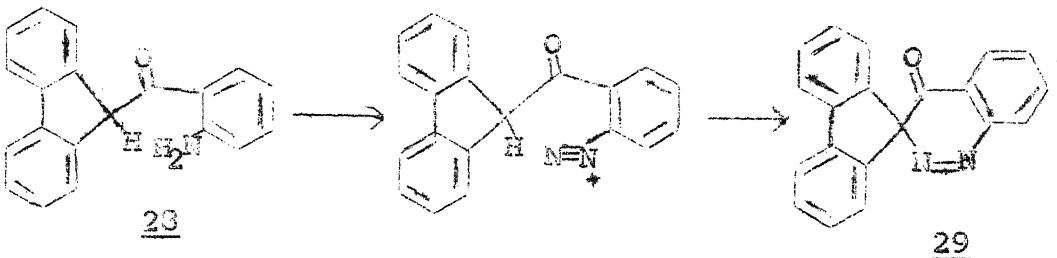


26



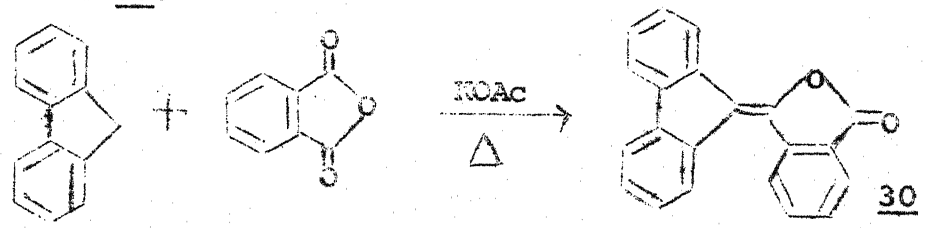
27

Compound 28 was chosen as a key intermediates towards model 29:



28 29

In view of the marked acidity of 9-benzoyl-9-fluorenyl proton it was hoped that the intramolecular coupling leading to 29 would be facile in buffered medium. The key intermediate 28 was sought from the known[35] and easily available fluorenylidine phthalide 30.*



30

* mp. 204–205° (lit.[35] mp 205–206°).
IR: ν_{max} (KBr) (cm^{-1}): 1770 (-C=O) and 975.

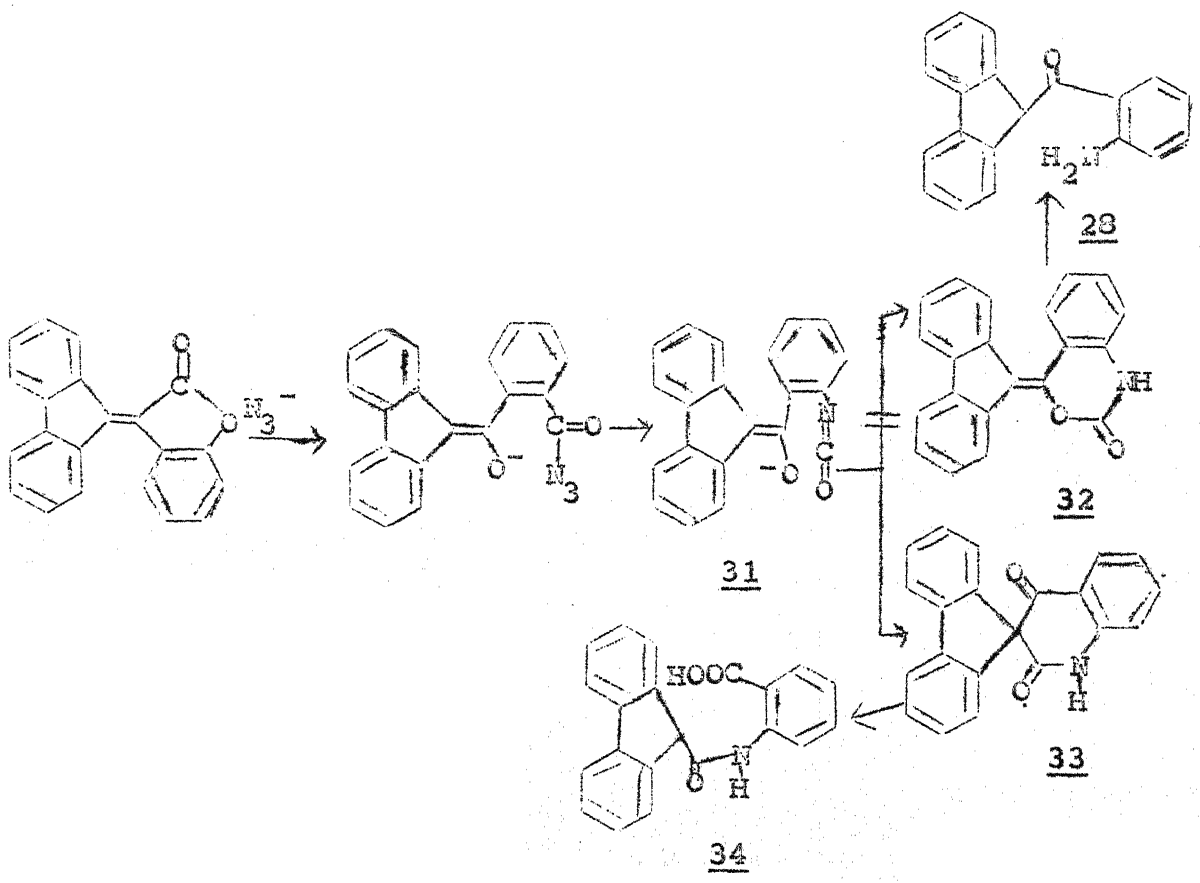
Reaction of 30 with sodiumazide in dimethylformamide was expected to lead to, via a Curtius rearrangement, species 31, that could undergo cyclization to 32 and which in turn could be expected to undergo ready hydrolysis to 28. However, in the event, the ambident ion 31 cyclized in an altornate manner to give 33. The structural assignment for 33* is based on IR, analysis and its ready transformation, in a predicted manner to give 34:**

---

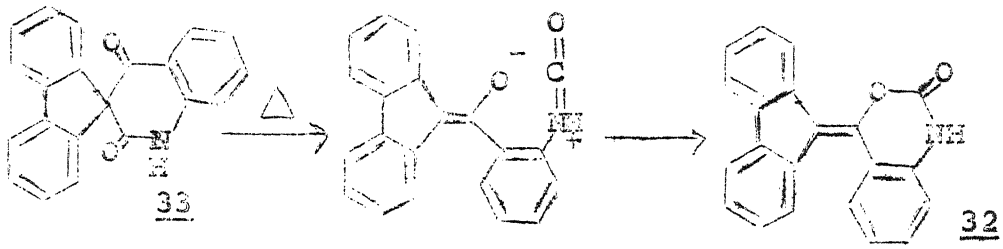
* 33, mp. 182-83°.

IR : ν_{max} (KBr) (cm^{-1}) : 3410, 1695 (-C=O) and 1380.

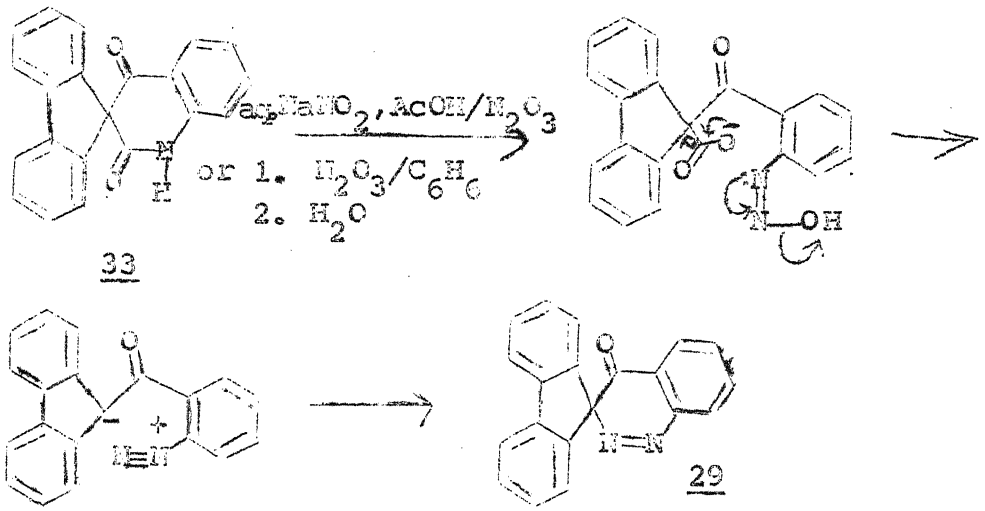
**34, mp. 132-33°.



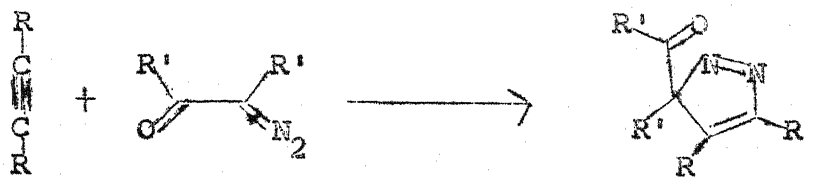
An attempt to transform 33 to the desired 32 thermally led to complete recovery of starting material.



Experiments to convert 33 directly to the model 29 by N-nitrosation also failed.

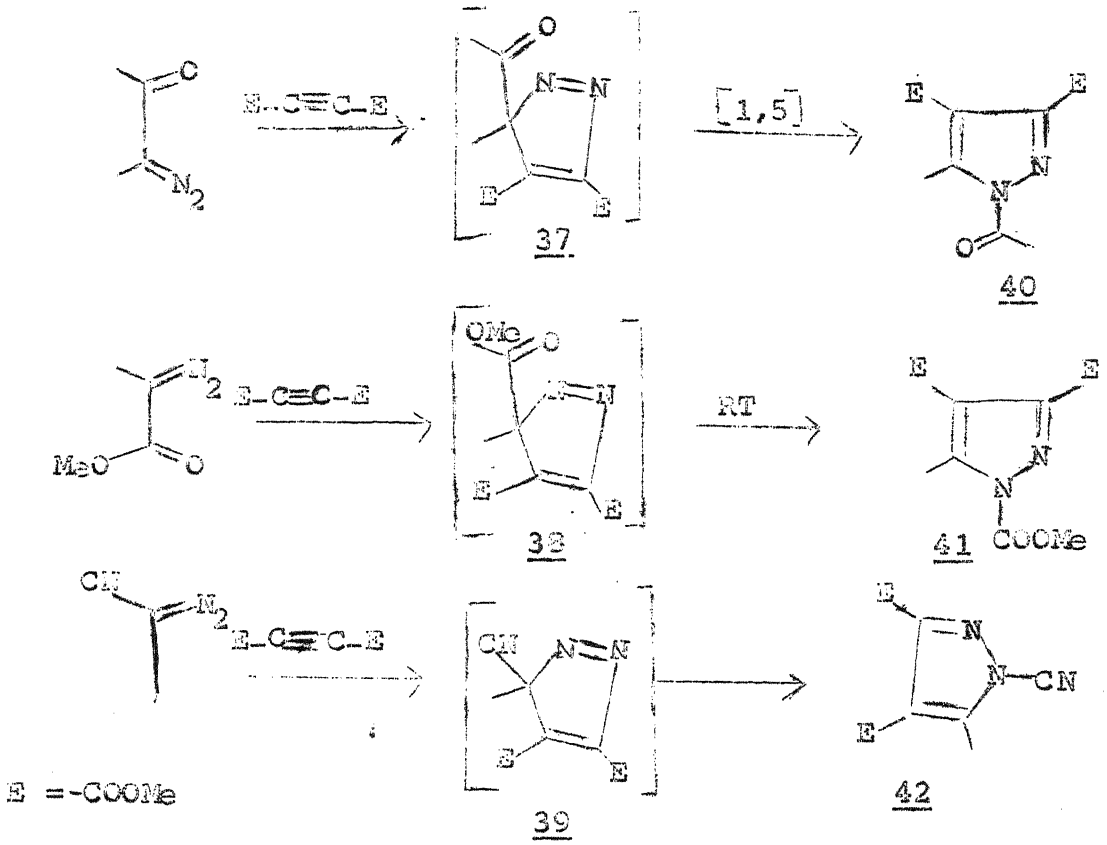


The system present in 2 namely 3H-pyrazole carrying carbonyl function at 3-position could be made by reaction of the corresponding diazoketones with acetylenic functions.

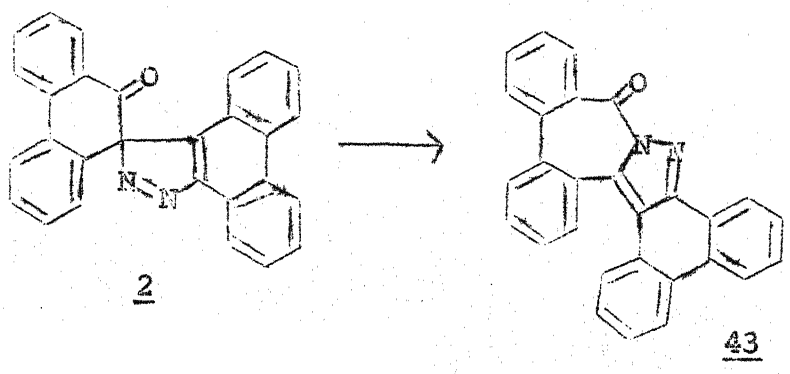


Very recently in 1972[36] three diazocarbonyl systems related to 35 have been added to acetylenedicarboxylic acid dimethyl ester.

In each case the initially formed adducts 37, 38 and 39 related to 36 underwent exceptionally easy thermal transformation to pyrazoles 40, 41 and 42 respectively. In retrospect, all the earlier claims pertaining to synthesis of systems related to 36 are suspect!



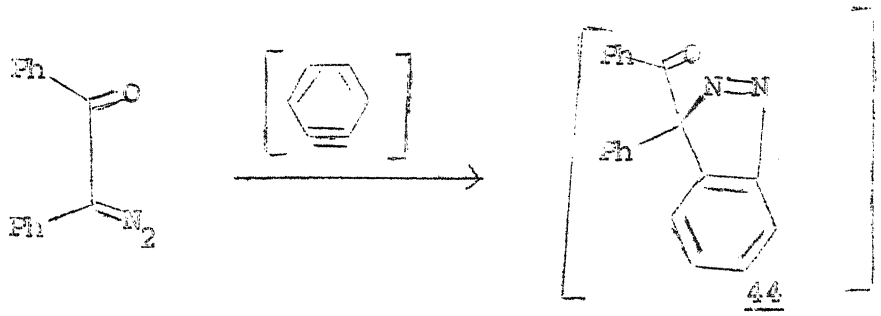
Further, in view of the high thermal stability of PQIA, structure 2 proposed by Hughes and Prankapralma[5] has to be revised outright to 43.



2 43

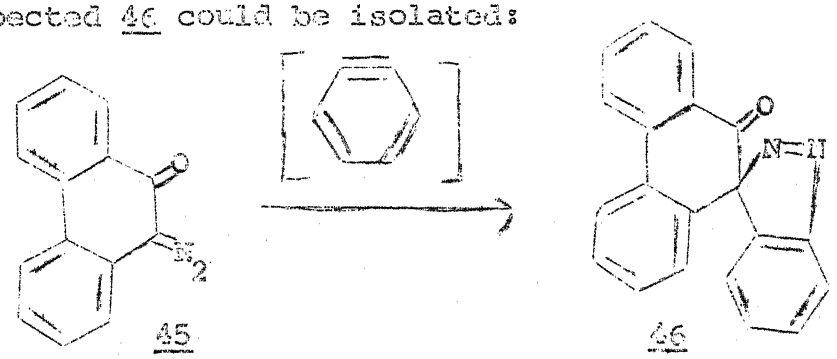
Such revision, however, will not alter the expectation based on hydrolysis, since 2 as well as 43 will give the same acid.

The present work relating to examination of 44 as a model of 2 was not fruitful because of the instability of the adduct. Compound 44 was prepared by a (4+2) addition of azibenzil and benzyne according to the reported procedure.[37] It was found that the product mp 162° (lit.[37] mp 167°) was not a single compound (TLC) and attempted crystallization from diverse solvent systems led to further complicated mixtures.



44

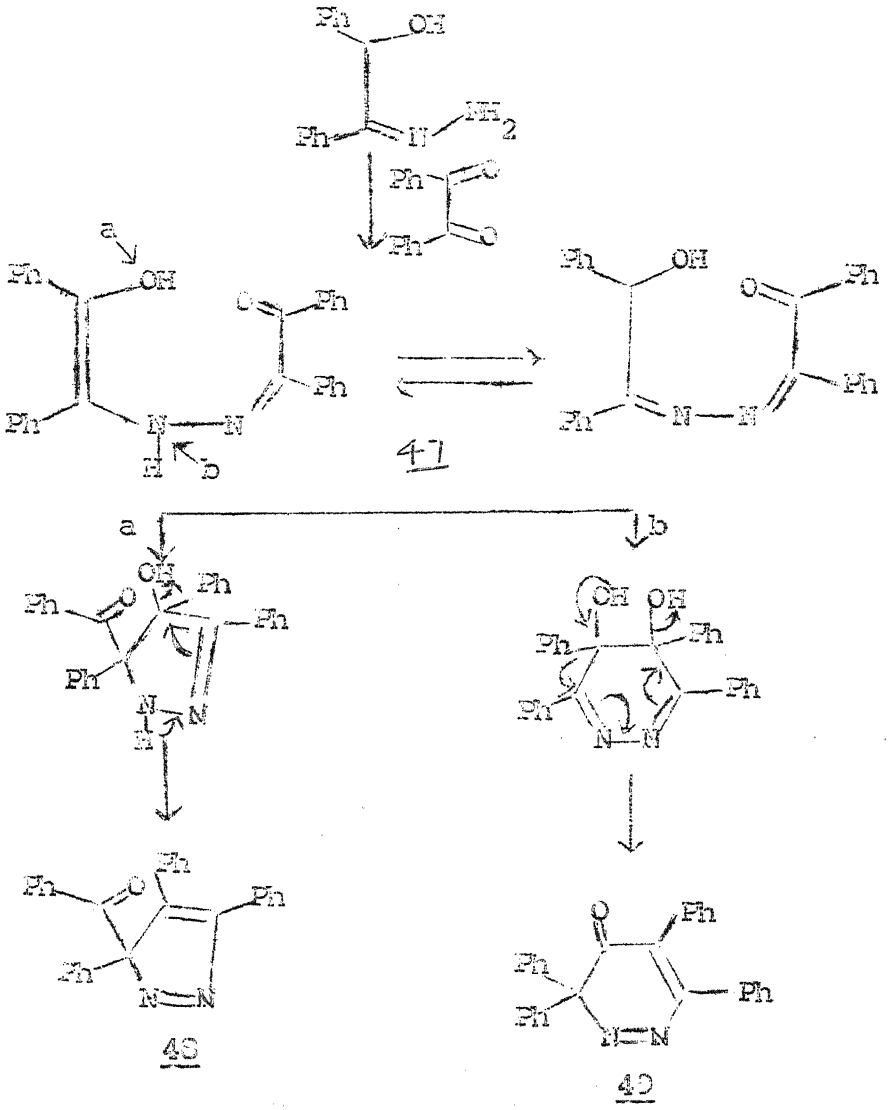
The attempted (4+2) addition involving benzyne and the diazoketone[39] 45 gave a complex mixture from which none of the expected 46 could be isolated:



45 46

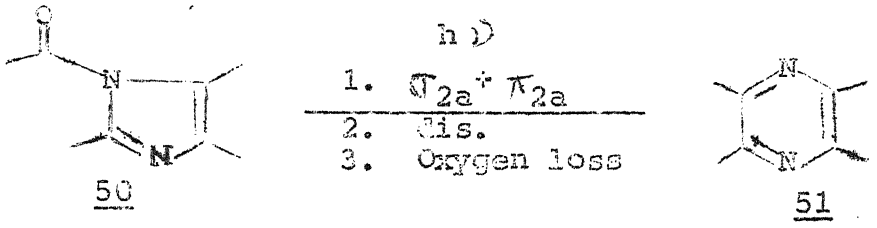
Another approach envisaged the generation of common-intermediate 47, by thermolysis of benzoinmonohydrazone with benzil, which could rearrange to either 48 or 49, these being

models of 2 and 3 respectively:



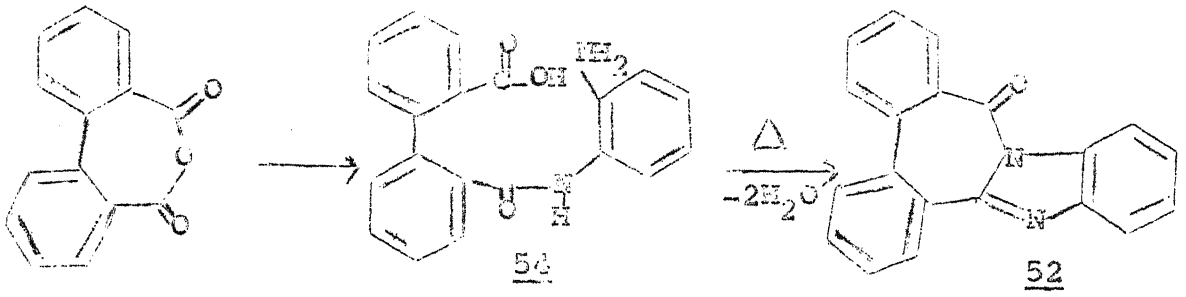
In the event benzoinmonohydrazone when reacted with benzil in o-dichlorobenzene gave crystalline material mp 208-210° which exhibited the expected benzoyl carbonyl absorption (IR). However, elemental analysis indicated a low nitrogen and high oxygen ratio and this substance has not been further examined.

With the identification of PQIA as 7 it became possible to study the novel PQIA → 13 change observed in the early phases of this work, with models related to PQIA. The essential features of this change can be exemplified on basis of structure 50.

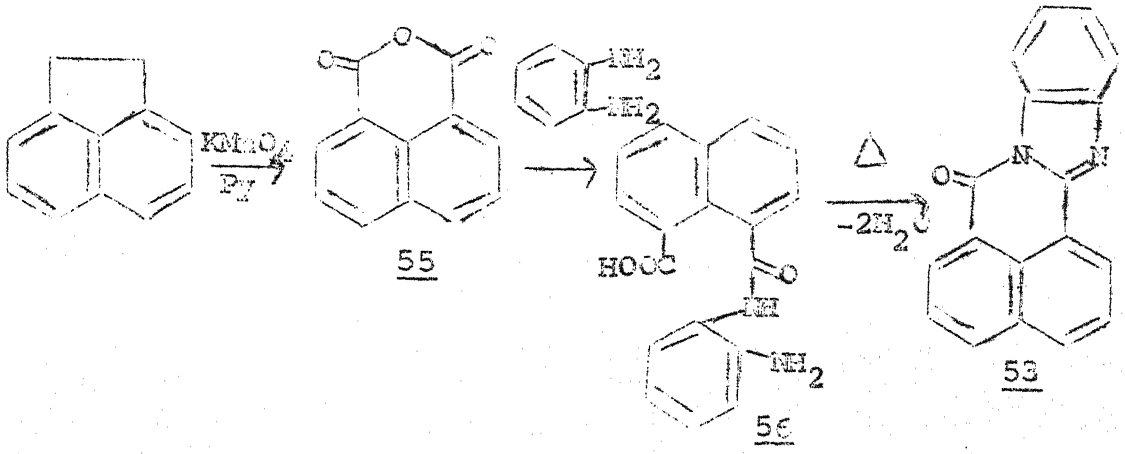


50 51

Models 52* and 53** closely related to PQIA were chosen for the photochemical studies and these were prepared according to reported procedures[39,40] via sequences outlined below:



54 52



55 56 53

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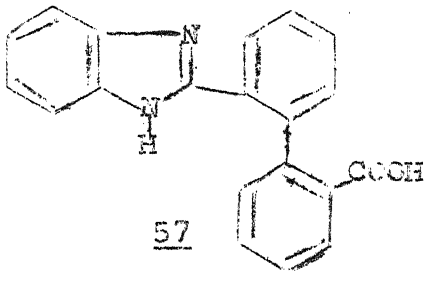
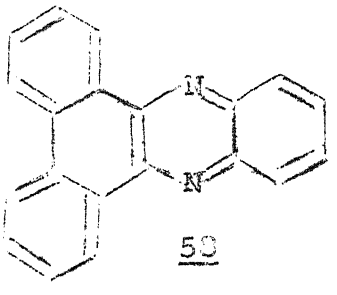
* 52, mp. 175-76° (lit.[39] mp 176-78°).
IR : ν_{max} (KBr) (cm^{-1}) : 1689 (C=O), 1433, 1325 and 943.

** 53, mp. 204-206° (lit.[40] mp 206°).
IR : ν_{max} (KBr) (cm^{-1}) : 1695 (C=O), 1351, 1316 and 770.

Photolysis of a THF solution of 52 using a Hanovia high pressure lamp for 10 hr caused no precipitation and work-up involving chromatography over silica gel gave compound mp 154-55° which has been tentatively identified, on basis of IR and analysis, as 57, arising from hydrolysis of unchanged 52 in the column. The expected dibenzophenazine 58 was prepared and TLC comparison clearly showed that none of 58 was present in the crude reaction mixture arising from photolysis.

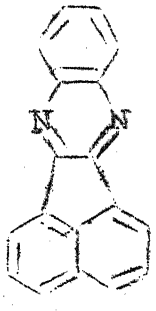


57



58

Photolysis of THF solutions of model 53 under these conditions caused no change (TLC). Here again the expected pyrazine 59 was prepared. TLC examination showed none of 59 in the reaction mixture.

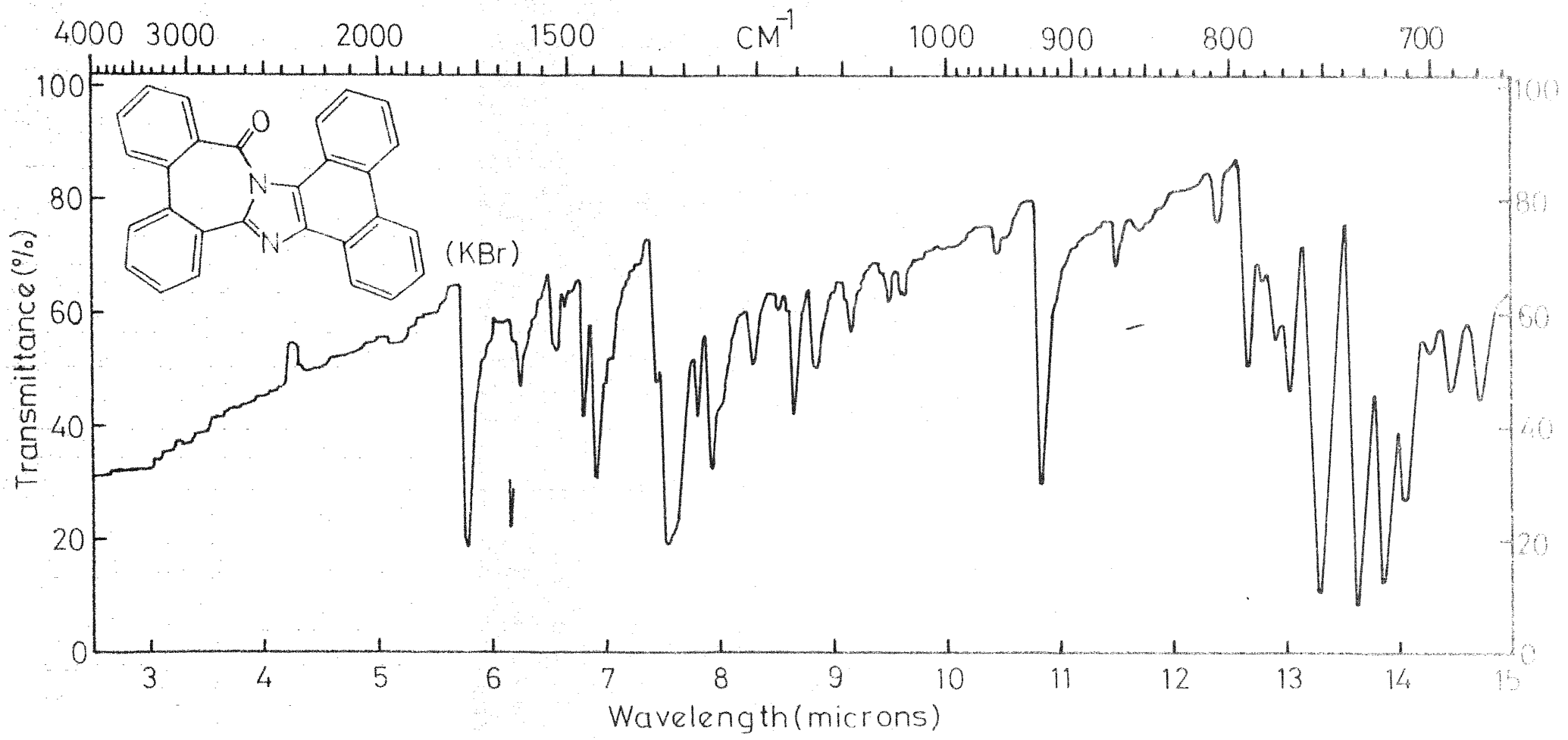


59

The behaviour of PQIA in contrast to models 52 and 53 can be accounted on basis of operation of many subtle factors such as specific excitation and insolubility of 13. Detailed examination of the photochemical properties of related systems[41]

have shown operation of diverse pathways as a function of substitution and solvents.

Finally photolysis of phenanthraquinonemonoimine itself in THF gave a complex mixture of products which contained neither the tetrabenzophenazine[19] nor PQIA.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100
80
60
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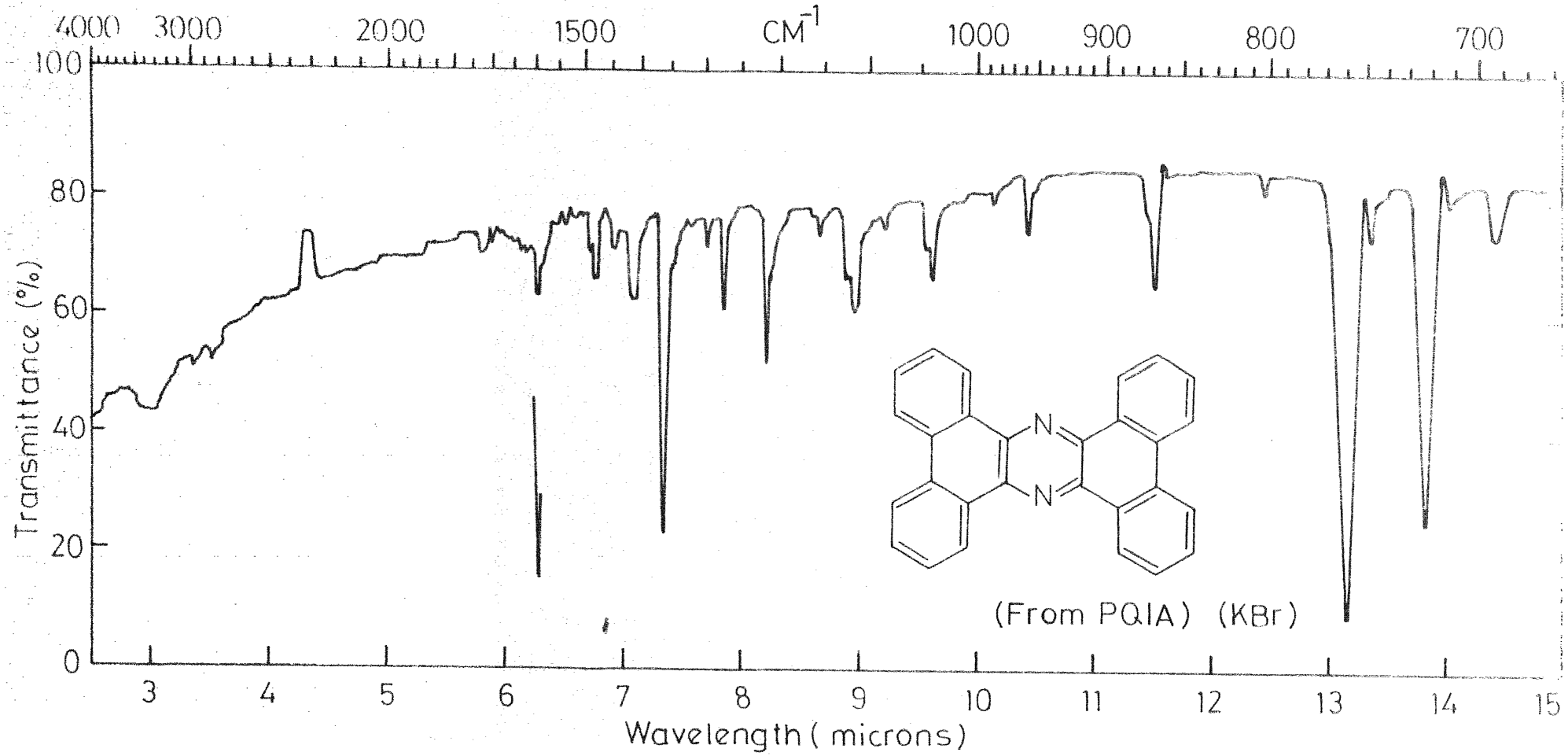
20
0
Transmittance (%)
O
N
N
(KBr)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)


4000
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CM-1
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700
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60
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20
0
Transmittance (%)
3
4
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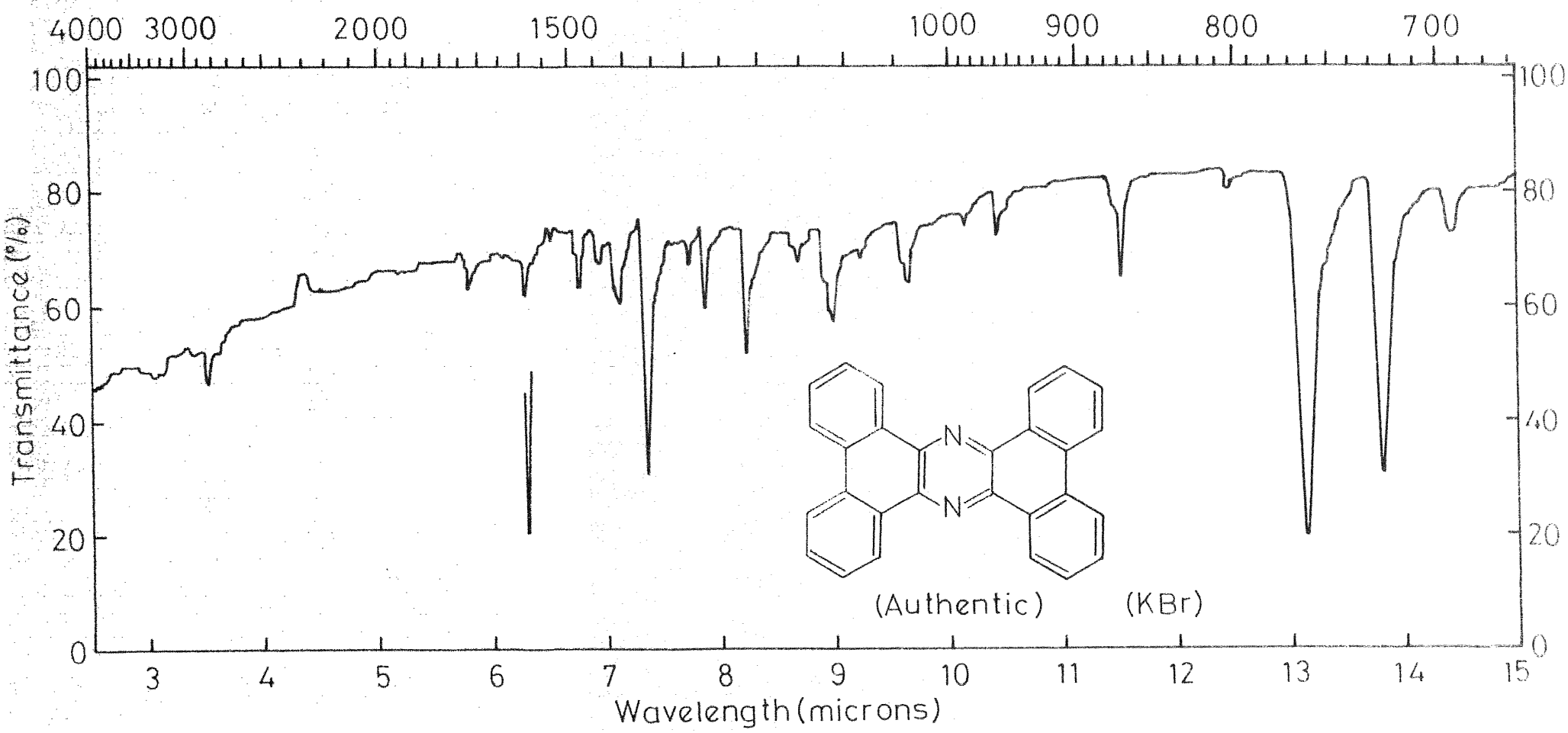
6
7
8
9
10
11
12
13
14
15
Wavelength (microns)
N
N
(From PQIA) (KBr)


4000 3000 2000 1500 1000 900 800 700
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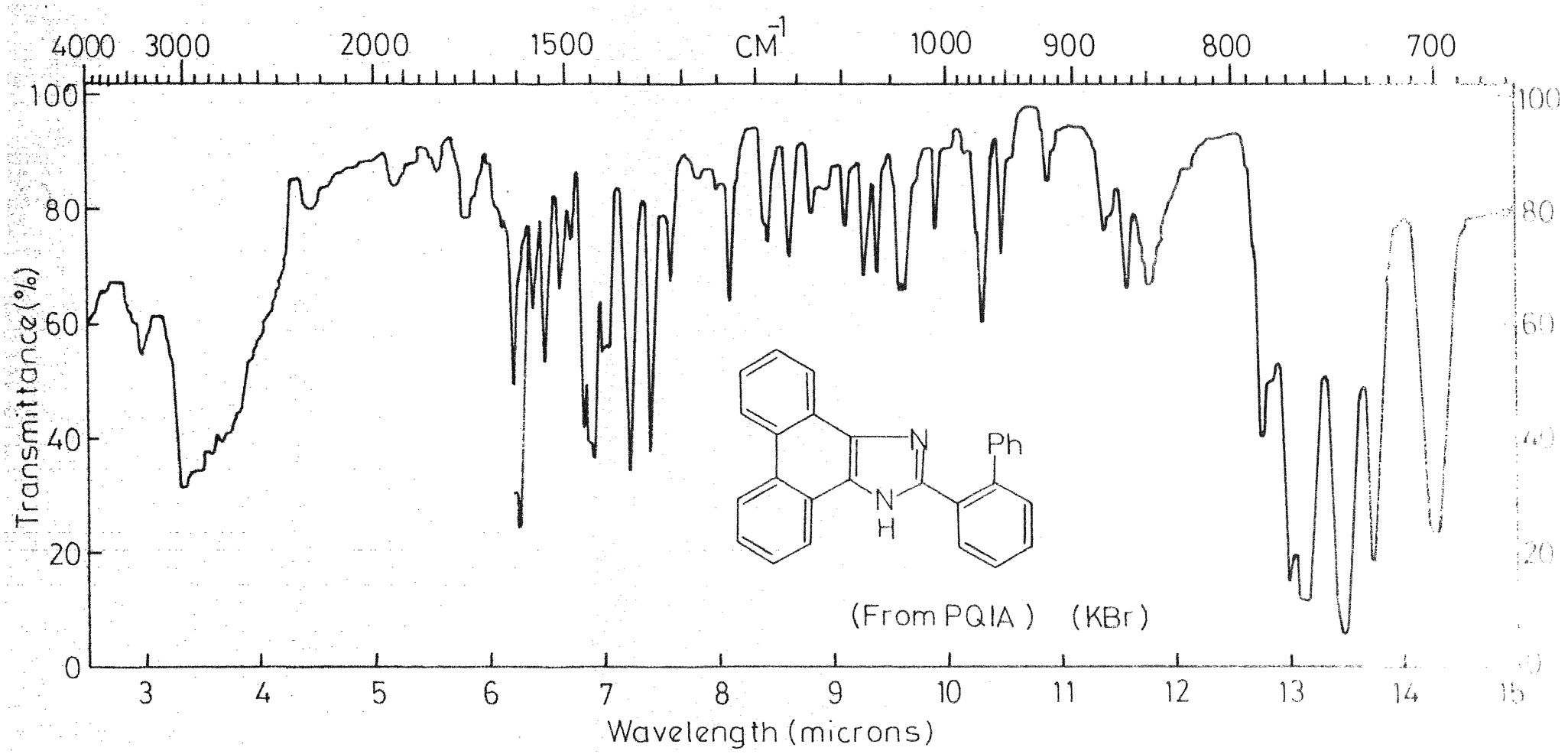
Transmittance (%)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)
N
N
(Authentic) (KBr)


4000
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CM⁻¹
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700
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80
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Transmittance (%)
N
Ph
N
H
(From PQIA) (KBr)
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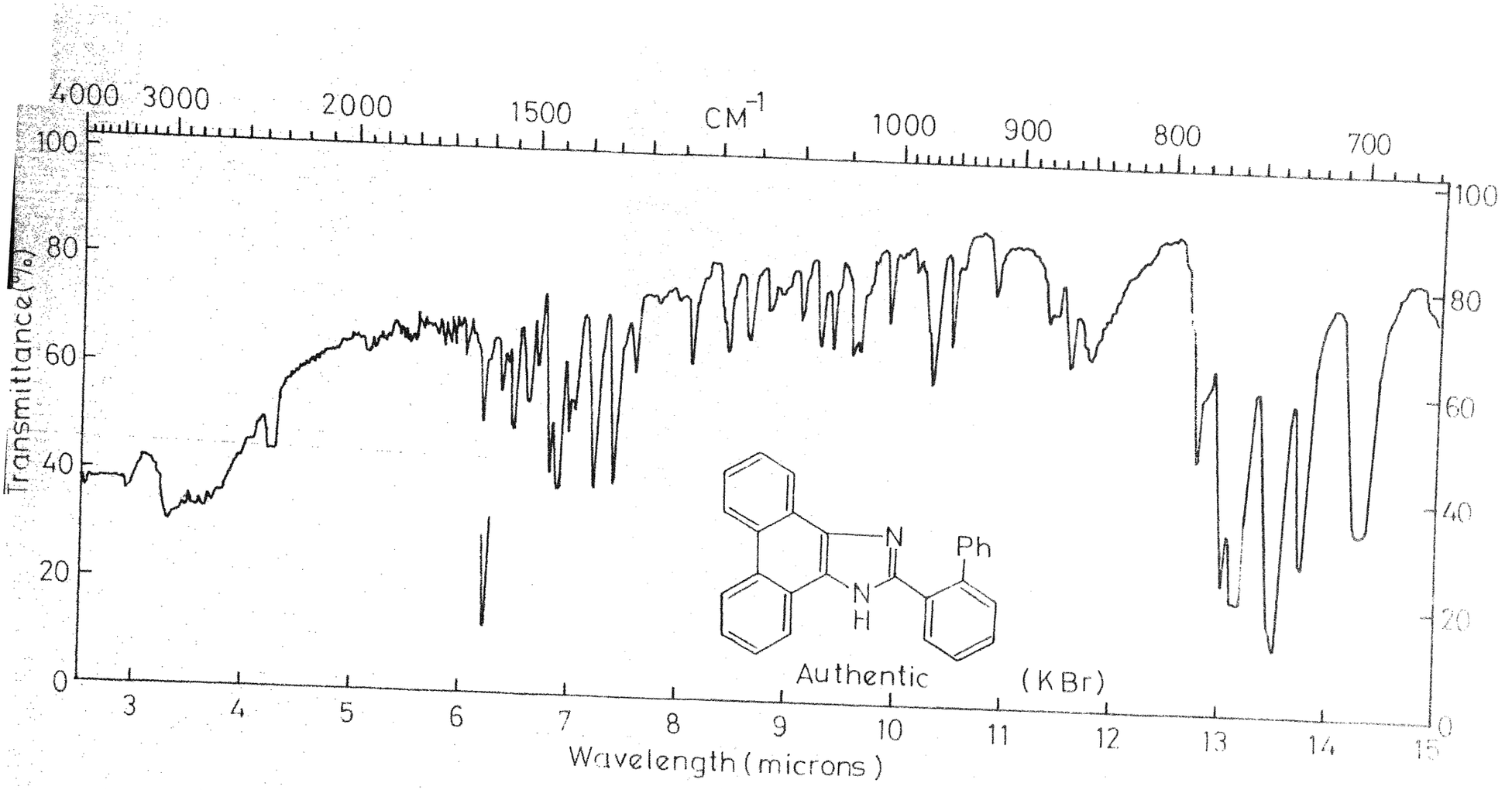
13
14
15
Wavelength (microns)


4000 3000 2000 1500 CM^{-1} 1000 900 800 700
Transmittance(%)
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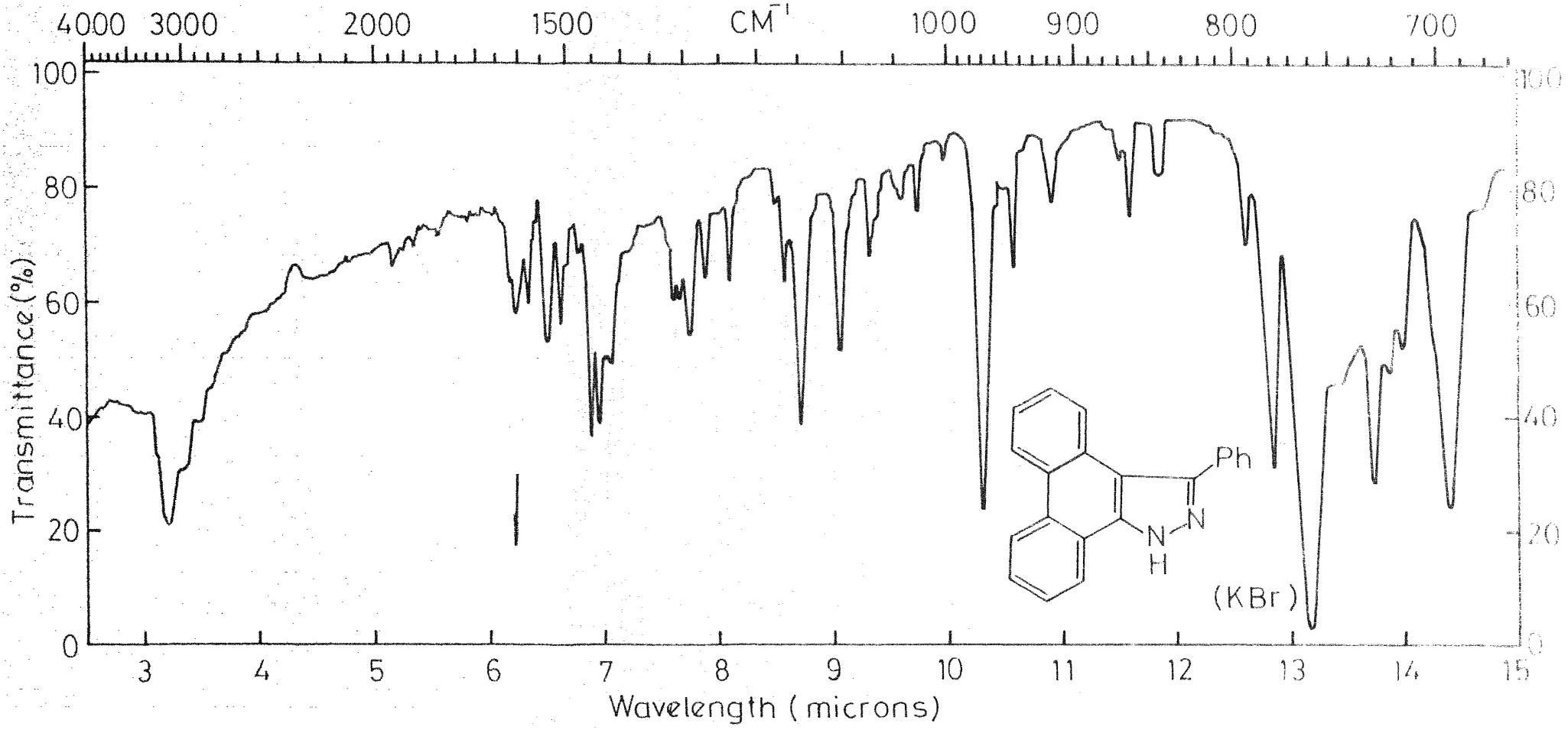
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)
N
Ph
N
H
Authentic (KBr)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100
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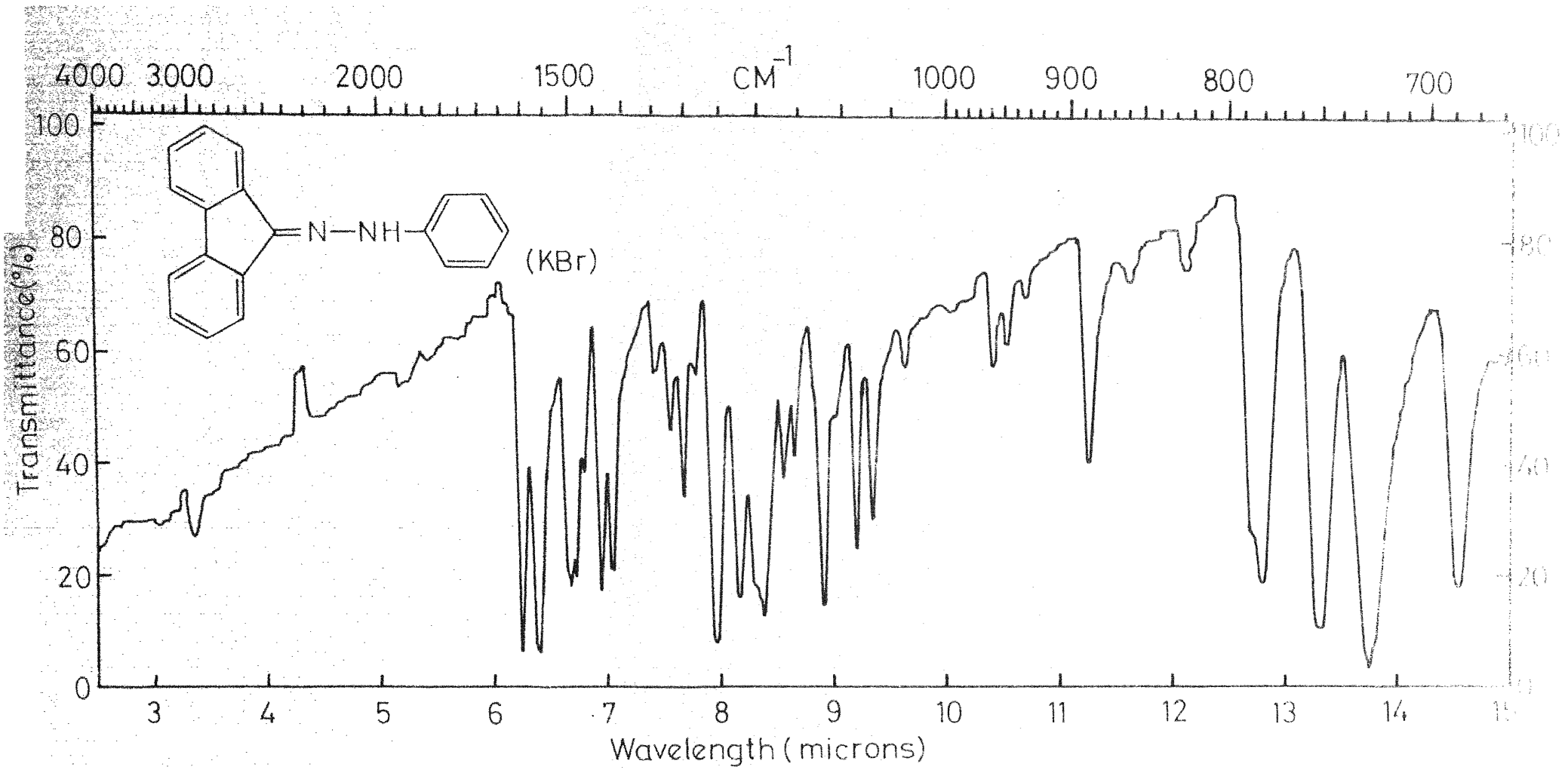
Transmittance (%)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)
Ph
N
N
H
(KBr)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100
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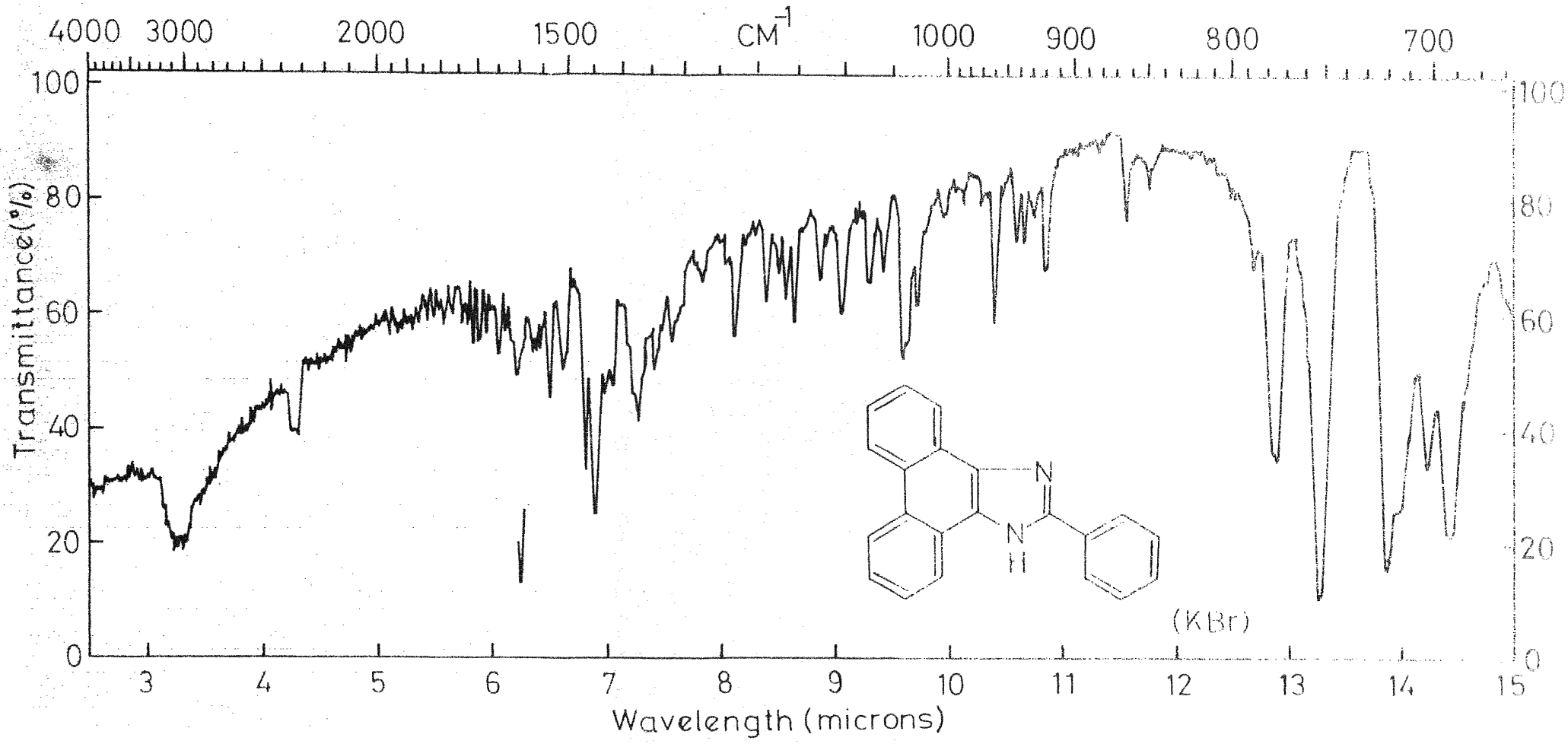
Transmittance(%)
N—NH
(KBr)
3 4 5 6 7 8 9 10 11 12 13 14
Wavelength (microns)


4000 3000 2000 1500 CM-1 1000 900 800 700
100
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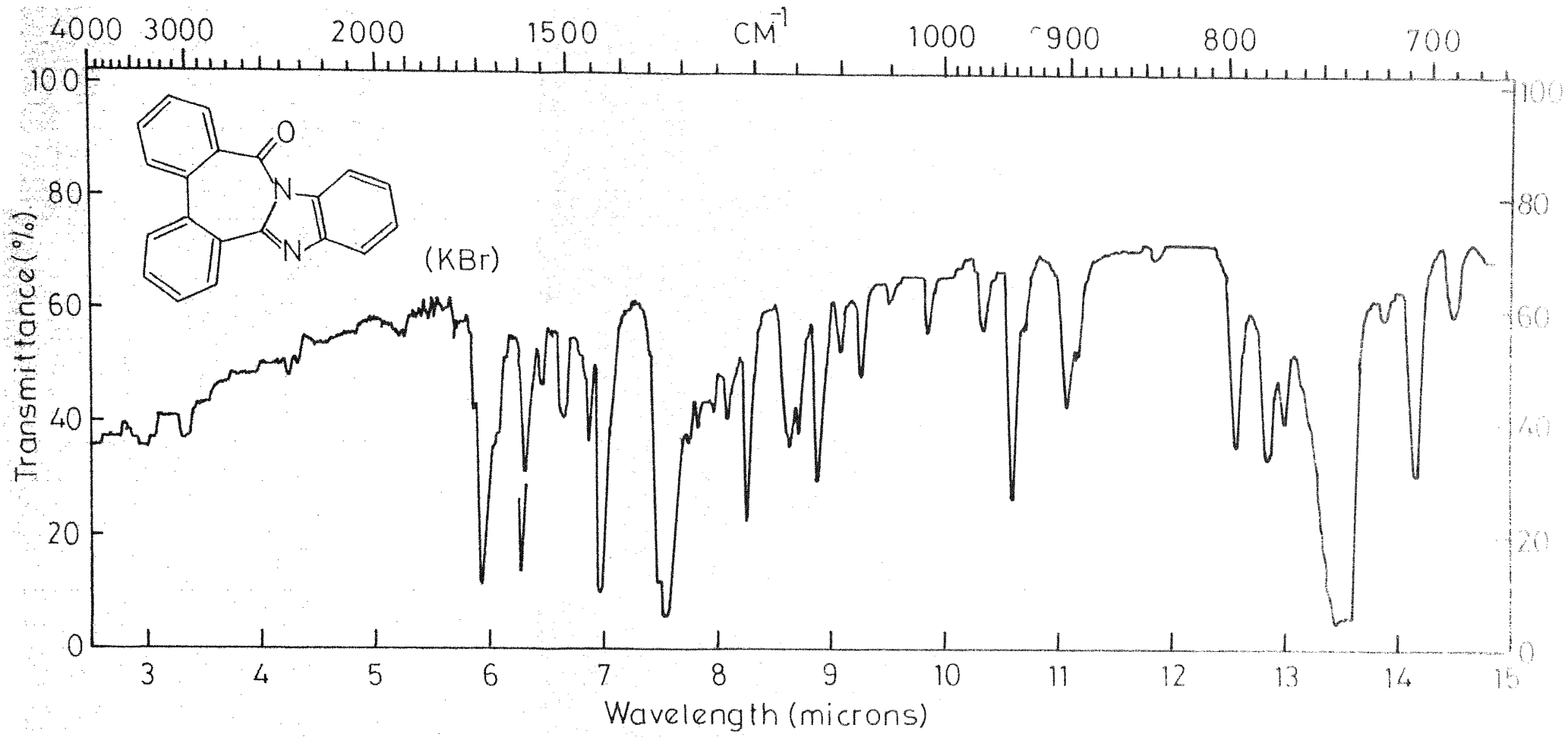
Transmittance(%)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)
N
N
H
(KBr)


4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
100
80
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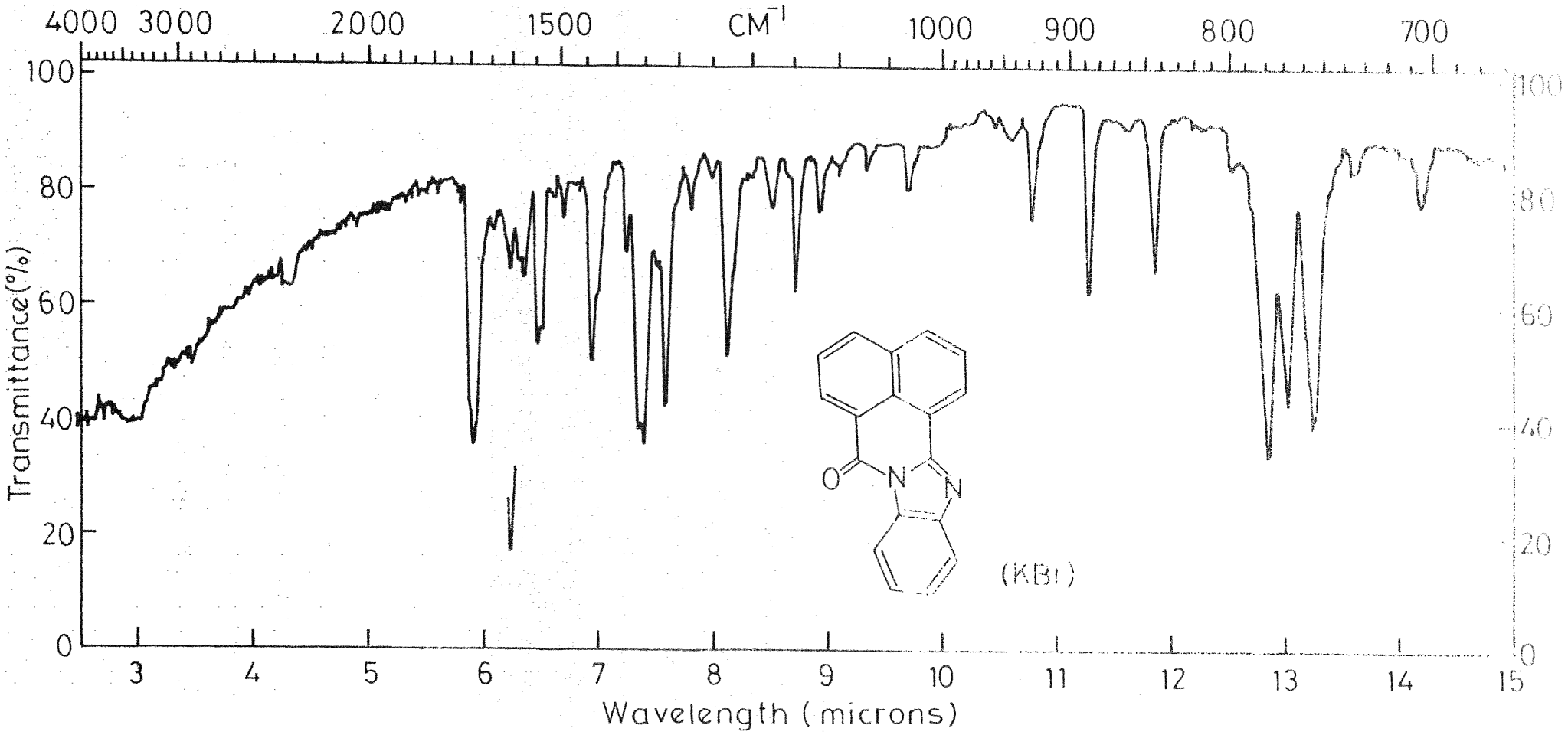
0
Transmittance (%)
(KBr)
O
N
N
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)


4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
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0
Transmittance(%)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)
O
N
N
(KBr)

I.E EXPERIMENTAL

GENERAL

Melting points are uncorrected and were determined on Fisher-John melting point apparatus. IR spectra were recorded on Perkin-Elmer 521 infrared spectrometer and Perkin-Elmer 137 infracord. Ultraviolet spectra were recorded on a Cary-14 spectrometer. Silica gel G (Stahl) was used for thin layer chromatography and column chromatography was done on silica gel (BDH), columns being prepared from its slurry in petroleum ether (60-80°).

Phenanthrenequinone[42]

To a stirred mixture of phenantrhene (100 g, 0.56 mol) and chromic acid (210 g, 2.1 mol, 1 litre) contained in a 3 litre 3 necked flask equipped with a reflux condenser and 1 litre dropping funnel was added conc. sulphuric acid (450 ml) at such a rate that gentle boiling was induced. After careful addition of a second lot (210 g, 2.1 mol) of chromic acid in water (500 ml) the reaction mixture was boiled under reflux for 0.3 hr, cooled, poured onto cold water and chilled to 10° in an ice bath. The crude precipitate was collected, washed free of acid and washed with (3 x 300 ml) of boiling water to remove diphenic acid. The crude quinone was triturated with 40% sodium bisulphite solution (4 x 300 ml) and filtered, the filtrate cooled to 5° and the adduct collected, suspended in water (300 ml) and treated with saturated sodium carbonate solution (500 ml). The resulting deep orange phenanthrenequinone was filtered by suction, washed

several times with cold water and dried on a porcelain plate. Crystallization from 95% ethanol gave 42 g (33%) of phenthrenequinone, mp 207-209° (lit.[42] mp 208-210°).

Phenanthraquinonemonoimine (1)

Ethanol (200 ml) was saturated with ammonia at 0°. Finely ground phenanthrenequinone (6 g, 0.03 mol) was then added and the suspension left stirred for 48 hr during which the reaction mixture was allowed to attain room temperature. The crude imine was filtered and crystallized from 95% ethanol to give 3.4 g (56%) of 1, mp 158-160° (lit.[5,6] mp 159-160°).

IR: ν_{max} (KBr) (cm^{-1}): 1661 (C=O), 1580, 1441 and 1275.

Phenanthraquinoneimideanhydride (7)

(i) A o-dichlorobenzene solution of phenanthraquinoneimine (4.0 g, 0.02 mol, 15 ml) was distilled slowly during overnight to enable removal of water. The hot mixture was cooled, diluted with petroleum ether (bp 40-60°), (30 ml), filtered and the residue refluxed in methanol/chloroform (1:1, 20 ml) to remove the unreacted phenanthraquinoneimine. The crude anhydride was crystallized from pyridine and dried to give 0.965 g (25 %) of 7, mp 260-261° (lit.[5] mp 257°).

Anal. Calcd for $C_{28}H_{16}N_2O$: C, 84.8; H, 4.0; N, 7.2. Found: C, 84.84; H, 4.08; N, 6.93.

IR: ν_{max} (KBr) (cm^{-1}): 1712 (C=O), 1441, 1323 and 921.

TLC: Single spot R_f: 0.65 (Benzene:Ethyl acetate, 50:50).

(ii) Phenanthraquinoneimine (4 g, 0.02 mol) in distilled aceticanhydride (12 ml) was heated under reflux for 0.15 hr. The hot mixture was filtered and the crude residue was crystallized from pyridine to give yellow needles of the imide-anhydride 7 (0.96 g, 25%), mp 256-258°(lit.[5] mp 257°).

Photolysis of Phenanthraquinoneimideanhydride: Isolation of Tetrabenzophenazine (13)

Pure phenanthraquinoneimideanhydride (0.96 g, 0.0025 mol, mp 260-261°)in distilled dry THF (350 ml) was photolyzed under nitrogen atmosphere employing Hanovia high pressure 450 watt lamp and with a vycor filter. After irradiation of 2 hr a yellow solid separated and the reaction mixture became turbid. After additional 6 hr photolysis the yellow solid was collected and crystallized from benzene (1 litre) to give 0.186 g (20%) of tetrabenzophenazine, mp $>420°$.

Anal. Calcd for $C_{28}H_{16}N_2$: C, 88.42; H, 4.2; N, 7.38. Found: C, 88.68; H, 4.41; N, 7.38.

IR: ν_{max}(KBr) (cm^{-1}): 1372, 1220, 755 and 720.

The sample was identical (IR) with an authentic tetrabenzophenazine prepared from phenanthrenequinone and acetamide.[28]

Preaparation of Authentic Tetrabenzophenazine (13)[28]

In a sealed tube a mixture of phenanthrenequinone (1 g, 0.005 mol), acetamide (1 g, 0.02 mol) and acetic acid (1 ml) was heated at 230-240°for 6-8 hr. The tube was cautiously opened

and the contents filtered. The residue was washed with ether and crystallized from nitrobenzene to give 0.463 g (48%) of the tetrabenzophenazine, mp $> 420^{\circ}$.

Reaction of Phenanthraquinoneimideanhydride with Boron Trifluoride Etherate: Attempted Isolation of Furan(9)

To a solution of phenanthraquinoneimideanhydride (0.1 g, 0.0002 mol) in dry benzene (10 ml) was added freshly distilled boron trifluoride etherate (4-5 drops). The resulting precipitate was boiled with ethanol for 0.5 hr, filtered and the filtrate on concentration gave a while solid (0.048 g) mp $223-225^{\circ}$. All the attempts to purify this material was unsuccessful.

IR: ν_{max} (KBr) (cm^{-1}): 3350-3150 (broad), 1645, 1448, 1290, 1050 (broad) and 750.

Reaction of Phenanthraquinoneimideanhydride with Saturated Methanolic Potassium Hydroxide : Isolation of 2-Phenanthrimidazolyl Biphenyl-2'-carboxylic acid

A suspension of PQIA (0.5 g, 0.0012 mol) in saturated methanolic potassium hydroxide (5 ml) was left stirred overnight at room temperature and then refluxed for one hr. The reaction mixture was cooled, treated with hydrochloric acid (6N, 15 ml), the precipitated acid filtered, washed several times with water and dried in vacuo to give 0.42 g (70%) of the acid as a white amorphous solid, mp $> 315^{\circ}$.

The insolubility of the acid in common solvents precluded further purification.

IR: ν_{max}(KBr) (cm^{-1}): 3000-2500 (diffused absorption), 1667 (-C=O).

Decarboxylation of the 2-Phenanthrimidazolyl-biphenyl-2'-carboxylic acid : Isolation of 2-Biphenylylphenanthrimidazole (17)

A mixture of the 2-phenanthrimidazolyl-biphenyl-2'-carboxylic acid (0.3 g, 0.0075 mol), copper powder (0.15 g, 0.0025 mol) and freshly distilled quinoline (5 ml) was refluxed at 240-250° for 2 hr. The suspension was poured over ice, extracted with ether and the ethereal extract washed several times with water and dil. hydrochloric acid. The combined aqueous layer when allowed to stand overnight deposited crude 17 (0.065 g) which on crystallization from benzene/hexane gave 0.055 g (20%) of the pure imidazole (17), mp 230°.

Anal. Calcd for $C_{27}H_{18}N_2$: C, 87.56; H, 4.86; N, 7.58. Found: C, 87.64; H, 5.07; N, 7.38.

IR: ν_{max}(KBr) (cm^{-1}): 1610, 1455 and 1445.

MS: m/e 370.

UV: λ_{max}(EtOH) (ϵ): 357 (2716), 340 (2808), 303 (8045), 284 (18025), 257 (68307), and 229 (32250) nm.

UV: λ_{max}(EtOH, H^+): 344 and 328 nm.

TLC: Single spot R_f: 0.80 (Methanol).

Preparation of Model Compound 18

Phenylacetylene

(i) Cinnamic acid dibromide:[43] To a stirred and refluxing carbon tetrachloride solution of cinnamic acid (37 g, 0.25 mol, 250 ml) was added gradually bromine (40 g, 0.25 mol) in carbon tetrachloride (25 ml) over 0.75 hr. After additional 0.25 hr the mixture was cooled and the colourless shining needles of the dibromide collected, mp 199°(d) (lit.[43] mp 202-205°), yield 70 g (93%).

IR: ν_{max} (KBr) (cm^{-1}): 3030-2500 (diffused), 1718.

(ii) Phenyl propiolic acid:[44] In an open dish, under stirring cinnamic acid dibromide (50 g, 0.16 mol) in 25% methanolic potassium hydroxide (2 x 100 ml) was heated on a water bath. The solvent was allowed to evaporate and the resulting thick paste was treated with methanol (150 ml) and the second lot was also allowed to evaporate. The pale yellow grannular product was cooled, filtered, washed with chilled methanol (3 x 10 ml), dissolved in ice water (1 l.) and made acidic with dil. hydrochloric acid (6N). The mixture was left aside in the ice-chest, the separated acid filtered and crystallized from hot carbon tetrachloride to give 16.5 g (65%) of the desired phenylpropiolic acid, mp 136-138°(lit.[44] mp 136-138°).

IR: ν_{max} (KBr) (cm^{-1}): 3030-2500 (broad), 2203 (-C≡C), and 1684 (-C=O).

(iii) Phenyl acetylene: An intimate mixture of phenylpropiolic acid (15.0 g, 0.1 mol) and barium hydroxide (7.85 g) was heated at 225-230° for 4 hr. The resulting mixture was distilled to give phenyl acetylene 8.2 g (78%), bp 70-75°/80 mm (lit.[44] bp 73-74°/80 mm).

Reaction of 9-Diazofluorene with Phenylacetylene : Isolation of (18)

A mixture of 9-diazofluorene (III.E) (0.192 g, 0.001 mol) and phenyl acetylene (0.4 g, 0.004 mol) was left aside at room temperature for 15 days. The deposited crystals were collected and crystallized from benzene to give 0.125 g (38%) of the indazole 18, mp 244-245° (lit.[31] mp 245-246°).

IR: ν_{max} (KBr) (cm^{-1}): 1400 and 975.

UV: λ_{max} (EtOH) (ϵ): 340 (2100), 330s (1400), 323 (2100), 253 (84000) and 223s (26000) nm.

UV: λ_{max} (EtOH, H^+): 339, 330 and 323 nm.

Preparation of Fluorenone Phenylhydrazone (19)

To a warm solution of fluorenone (1.8 g, 0.01 mol) in 95% ethanol (15 ml) was added dropwise phenylhydrazine (1 g, 0.01 mol) and the resulting mixture was heated with a catalytic amount of acetic acid. The phenylhydrazone which separated on cooling was collected and crystallized from ethanol to give 2.16 g (90%) of 19, mp 148-150° (lit.[32] mp 151°).

IR: ν_{max} (KBr) (cm^{-1}): 1600, 1560, 1497 and 1255.

UV: λ_{max} (EtOH) (ϵ): 388 (35080) and 245 (72710) nm.

Preparation of 2-Phenyl-Phenanthrimidazole (20)[20]

A solution of phenanthrenequinone (1.04 g, 0.005 mol) and ammonium acetate (7.8 g, 0.1 mol) in hot glacial acetic acid (10 ml) was treated with distilled benzaldehyde (0.55 g, 0.005 mol) in glacial acetic acid (5 ml). The reaction mixture was refluxed for one hr, cooled, diluted with water (75 ml) and neutralized with liquor ammonia. The crude imidazole was collected and crystallized from alcohol to give 1.18 g (80%) of 2-phenyl-phenanthrimidazole (20), mp 312-314° (lit.[20] mp 314°).

IR: ν_{max} (KBr) (cm^{-1}): 1604 and 1450.

UV: λ_{max} (EtOH) (ϵ): 359 (8250), 344 (10900), 313 (19820), and 262 (59450) nm.

UV: λ_{max} (EtOH, H^+) : 349 and 335 nm.

TLC: Single spot R_f: 0.78 (Methanol).

Synthesis of 2-Biphenylyl Phenanthrimidazole (17)

(i) 2-Nitro diphenyl:[45] Concentrated nitric acid (160 ml, d, 1.5) was added in drops over 1.5 hr to a stirred mixture of diphenyl (100 g, 0.66 mol) and acetic acid (150 ml). The reaction mixture was cooled and the precipitated 4-nitrodiphenyl collected and the filtrate diluted with water and steam distilled to remove unchanged diphenyl. The non-volatile residue was distilled, bp 188-195°/20 mm. The distillate was dissolved in alcohol at 40° and the crystals of 4-nitro-diphenyl filtered. Concentration of the mother liquor gave 2-nitro diphenyl, 40 g (30%) mp 35-36° (lit.[45] mp 35-37°).

IR: ν_{max} (KBr) (cm^{-1}): 1538 ($-NO_2$, asym) and 1351 (NO_2, sym).

(ii) 2-Amino diphenyl:[46] To a solution of 2-nitro-diphenyl (7.5 g, 0.0375 mol) in alcohol (60 ml) was added a solution of stannous chloride (50 g, 0.26 mol) in conc. hydrochloric acid (50 ml). After refluxing the mixture over water bath for 3 hr, it was cooled, neutralized with cold dil. sodium hydroxide and the resulting mixture was extracted from ether. The ether extract was washed thoroughly with water, dried ($MgSO_4$) and evaporated. The residual liquid was distilled *in vacuo* at 120°/15 mm to give 3.8 g (59%) of pure 2-amino-diphenyl, mp 47-48° (lit.[46] mp 49-50°).

(iii) 2-Iodo diphenyl:[47] To a solution of 2-amino-diphenyl (3.5 g, 0.021 mol) in dil. hydrochloric acid (50%, 11 ml) was added aqueous sodium nitrite (1.5 g, 0.025 mol, 7 ml) and the solution was cooled to 0°. An aqueous solution of potassium iodide (10 g, 0.06 mol , 15 ml) was added slowly to the stirred reaction mixture. The resulting heavy paste was allowed to attain room temperature during 1.5 hr and the mixture warmed on a water bath to expel nitrogen. The reaction mixture was extracted with benzene and the organic layer washed with saturated sodium thiosulphate, water, dried ($CaCl_2$) and distilled at 110-122°/0.6mm (lit.[47] 158°/6mm) to give 3.3 g (60%) of 2-iodo-diphenyl.

(iv) 2-Formyl diphenyl:[33] Under nitrogen to a stirred solution of 2-iodo diphenyl (1.5 g, 0.005 mol) in dry ether (10 ml) was added magnesium strips (0.2 g, 0.005 mol). Instantaneous vigorous reaction! After 0.2 hr a solution of distilled N-methylformanilide (1.4 g, 0.001 mol) in ether (5 ml) was added

in drops and the mixture was left stirred at room temperature for 3 hr. The reaction mixture was made acidic with 6N hydrochloric acid (2 x 20 ml) and extracted from ether (3 x 20 ml). The ether extract was washed successively with water, sodium chloride, dried ($MgSO_4$) and evaporated to give 0.92 g (100%) of essentially pure 21 (TLC).

IR: ν_{max} (neat) (cm^{-1}): 1695 (-C=O).

(v) Reaction of phenanthrenequinone with 2-formyl-diphenyl : Synthesis of 2-biphenylyl phenanthrimidazole (17)
A solution of phenanthrenequinone (0.52 g, 0.0025 mol) and ammonium acetate (3.86 g, 0.0025 mol) hot glacial acetic acid (5ml) was treated with 2-formyl diphenyl (0.545 g, 0.003 mol) in 5 ml of acetic acid. The reaction mixture was refluxed for 1 hr, cooled, diluted with water (40 ml) and neutralized with liquor ammonia. The precipitate was collected, crystallized from benzene/hexane to give 0.85 g (92%) of 17, mp 223-224°.

IR: ν_{max} (KBr) (cm^{-1}): 1610, 1455 and 1445.

UV: λ_{max} (EtOH) (ϵ): 356 (2734), 341 (2842), 305 (8072), 285 (18074), 257 (68368) and 229 (32288) nm.

UV: λ_{max} (EtOH, H^+) : 344 and 328 nm.

This compound was identical in all respects (mp, IR and UV) with the decarboxylated product.

Attempted Preparation of 3-Spiro(3H)-fluorenyl), 4-oxa-dihydro-Cinnoline (29)

(i) Fluorenylidine phthalide:[35] An intimate mixture of sublimed phthalic anhydride (20 g, 0.14 mol), fluorene (24 g, 0.09 mol) and anhydrous potassium acetate (14 g, 0.14 mol) was heated in an oil bath at 200-220° for 2 hr. The brown residue was boiled with water, dried, pulverized, extracted with ether to remove unreacted fluorene and crystallized from a mixture of ethyl acetate and alcohol to give 2.5 g (7%) (lit.[35] 2.5 g, 7%) of fluorenylidine phthalide as beautiful yellow needles, mp 204-205° (lit.[35] mp 204-206°).

IR: ν_{max} (KBr) (cm^{-1}): 1770 (-C=O), and 995.

TLC: Single spot (R_f: 0.78, methanol).

(ii) Attempted preparation of 32: Isolation of 2,4-Dioxo-spiro(tetrahydro-quinoline-3,9'-fluorene) (33)

A stirred mixture of fluorenylidine phthalide (30) (0.5 g, 0.0017 mol), sodium azide (0.5 g, 0.0017 mol) and distilled DMF (5-6 ml) was heated in an oil bath at 160-170° for 5 hr, cooled and added to ice-cooled water (100 ml). The reaction mixture was extracted with ether, washed with water, dried ($MgSO_4$) and evaporated. The residue on crystallization from hexane gave beautiful yellow needles (0.140 g, 23%) of 33, mp 182-183°.

Anal. Calcd for $C_{21}H_{13}NO_2$: C, 81.2; H, 4.2; N, 4.5. Found: C, 81.4; H, 4.52; N, 4.42.

IR: ν_{max} (KBr) (cm^{-1}): 3410, 1695 and 1380.

Reaction of 33 with Methanoilic Potassium Hydroxide : Isolation of 34

A solution of 33 (0.05 g, 0.0016 mol) in methanolic potassium hydroxide (2.5 ml) was left aside overnight. The resulting mixture was concentrated, diluted with water and on acidification gave 34 (0.032 g, 65%), mp 132-133°.

Anal. Calcd for $C_{21}H_{15}NO_3$: C, 76.41; H, 4.5; N, 4.25. Found: C, 76.23; H, 4.38; N, 4.12.

Reaction of 33 with Sodium Nitrite/Hydrochloric acid : Attempted Preparation of Model 29

To an ice cooled (0°) stirred suspension of 33 (0.031 g, 0.0001 mol) in water (2-3 ml) was added aqueous sodium nitrite (0.065 g, 2 ml). Work-up gave unchanged starting material.

Reaction of 33 with Dinitrogen Trioxide in Benzene: Attempted Preparation of 29

A solution of dinitrogen trioxide in benzene was prepared by reaction of arsenious oxide with conc. nitric acid. To a stirred solution of 33 in benzene (0.029 g, 0.0001 mol, 3 ml) was added excess dinitrogen trioxide in benzene and the resulting solution was refluxed. TLC showed no change.

Pyrolysis of 33 : Attempted Isomerization to 32

A sample of 33 (0.02 g, ~0.0001 mol) was heated in an oil bath at 210° for 2 hr. The sublimed material was identical (TLC) with starting material.

the precipitated salt was collected, carefully washed with cold tetrahedrofuran and dried. Yield 2.29 g (61%).

(ii) Reaction of azibenzil with benzyne:[37] Benzene diazonium o-carboxylate (0.44 g, 0.003 mol) was added to a stirred solution of azibenzil (0.679 g, 0.003 mol) in dry methylene chloride (15 ml). The mixture was refluxed for 8 hr. The solvents were evaporated and the residue chromatographed on alumina using benzene as eluent. The crude product (mp (159-162°, 0.60 g, 67%) was not pure and attempted crystallization from solvents lead to further decomposition.

Attempted Preparation of Models 48 or 49 Involving Common Intermediate

(i) Benzoin hydrazone:[50] A solution of benzoin (10 g, 0.05 mol) in alcohol (100 ml) was heated over a water bath with hydrazine hydrate (3 g, 0.06 mol). The reaction mixture was cooled and crystals of crude hydrazone collected and crystallized from alcohol to give benzoin hydrazone (7.6 g, 67%), mp 72-73° (lit.[50] mp 72°).

IR: ν_{max} (KBr) (cm^{-1}): 1440, 1430, 1035 and 1020.

Reaction of Benzoin Hydrazone with Benzil in o-Dichlorobenzene

A solution of benzoin hydrazone (5.65 g, 0.025 mol) and benzil (5.25 g, 0.025 mol) in o-dichlorobenzene (20 ml) was heated in an oil bath at reflux overnight. The solvents removed in vacuo and the crude residue on trituration with petroleum ether (bp 40-60°) gave crystals mp 209-210°; yield 2.3 g.

Anal. Found: C, 78.34; H, 4.06; N, 5.50.

IR: ν_{max} (KBr) (cm^{-1}): 1675, 1590, 1445 and 1220.

Preparation of Dibenzo(c,e)benzimidazo(1,2c-a)izepin-9-one (52)

(i) Diphenic anhydride:[51] A stirred mixture of diphenic acid (7.25 g, 0.03 mol) and acetic anhydride (225 ml) was heated at 120° for 1 hr, cooled and the crystals of anhydride collected, washed with acetic acid and dried. Yield: 3.5 g (52%), mp 218-220° (lit.[51] mp 220°).

IR: ν_{max} (KBr) (cm^{-1}): 1773, 1745, 1300, 1073 and 1044.

(ii) Diphen-2''-aminoanilide carboxylic acid (54): A mixture of powdered diphenic anhydride (4.48 g, 0.02 mol) and o-phenylene diamine (2.16 g, 0.02 mol) in alcohol (60 ml) was refluxed for 0.5 hr, cooled, the crude 54 collected and dried to yield 2.65 g (40%), mp 125-130°.

(iii) Pyrolysis of diphen-2''-aminoanilide carboxylic acid (54): Isolation of (52): The adduct 54 (1 g, 0.003 mol) was heated to 150° in an oil bath for 0.5 hr. Heavy frothing! The reaction mixture cooled, acetic anhydride (25 ml) was added and the resulting mixture heated until solution was achieved and cooled. The precipitated crystals of 52 were collected and crystallized from ethanol to give 0.83 g (93%) of pure 52, mp 175-176° (lit.[39] mp 173°).

IR: ν_{max} (KBr) (cm^{-1}): 1689, 1433, 1325 and 943.

TLC: Single spot (R_f: 0.63 benzene:ethyl acetate, (50:50)

Photolysis of 52: Attempted Isolation of Dibenzophenazine (58)

Compound 52 (0.75 g, 0.0025 mol) in distilled dry THF (380 ml) was photolyzed using a Hanovia high pressure lamp for 10 hr using a vycor filter. THF was removed under reduced pressure and the crude product was chromatographed over silica gel. Elution with benzene/ethyl acetate gave compound 57 (0.235 g), mp 154-155°.

IR: ν_{max} (KBr) (cm^{-1}): 3333-2500 (broad), 1695, 1439 and 757 (broad).

Preparation of Dibenzophenazine (58)

To a hot solution of phenanthrenequinone (0.208 g, 0.001 mol) in glacial acetic acid (5 ml) was added ethanolic solution of o-phenylene diamine (0.094 g, 0.001 mol, 5 ml). Instantaneous colour change! The resulting precipitate was filtered, washed free of acid, dried and crystallized from hot alcohol to give 0.213 g (76%) of the pure phenazine, mp 219° (lit.[52] mp 217°).

Preparation of 1,2-Naphthoylenebenzimidazole (53):[40]

(i) Naphthalic anhydride:[53] To a mixture of technical grade acenaphthene (7.7 g, 0.05 mol) in pyridine (140 ml) was added a solution of potassium permanganate (35.5 g, 0.225 mol, 140 ml) and the mixture heated at 60° for 1 hr, cooled, treated successively with sodium thiosulphate, sulphuric acid (dilute, 6N) and then extracted with methylene chloride. The organic layer was washed with aqueous sodium bicarbonate, dried ($MgSO_4$) and evaporated. The crude residue was crystallized from a mixture of

alcohol and benzene to give 3.75 g (38%) of naphthalic anhydride mp 267-268°(lit.[53], mp 268°).

IR: ν_{max}(KBr) (cm^{-1}): 1770, 1740 (-C=O), 1020 and 780.

(ii) Reaction of naphthalic anhydride with o-phenylene-diamine: Isolation of N-(o-aminophenyl)naphthalimide-8-carboxylic acid (56): A mixture of o-phenylene diamine (1.08 g, 0.01 mol) and naphthalic anhydride (1.98 g, 0.01 mol) in methanol (15 ml) was heated at 60° for 4 hr, cooled and the crude product collected, washed successively with methanol (2-3 ml), aqueous sodium carbonate (5-6 ml) and crystallized from benzene to give 2.12 g (69%) of 56, mp 270-272°(lit.[40] mp 270-272°).

(iii) Pyrolysis of N-(o-aminophenyl)naphthalimide-8-carboxylic acid(56):Isolation of 1,2-naphthoylenebenzimidazole(53): The naphthalimide carboxylic acid (56) (2 g, 0.006 mol) in acetic acid (15 ml) was heated under reflux for 1 hr, cooled and the brilliant yellow compound was crystallized from methanol to give 0.85 g (50%) of pure 53, mp 204-206°(lit.[40] mp 206°).

IR: ν_{max}(KBr)(cm^{-1}): 1695 (-C=O), 1351, 1316 and 778.

TLC: Single spot (R_f: 0.55, benzene:ethyl acetate,50:50).

Photolysis of 1,2-Naphthoylenebenzimidazole (53):Attempted Isolation of the Azine 59

Compound 53 (0.6 g, 0.0022 mol) in distilled THF (350 ml) was photolyzed using a Hanovia high pressure lamp for 8 hr. TLC examination showed no change.

Acenaphthenequinone[54]

To a stirred mixture of technical grade acenaphthene (20g, 0.13 mol), ceric acetate (1 g) and glacial acetic acid (160 ml) was added sodium dichromate dihydrate (65 g, 0.22 mol) over a period of 2 hour. The temperature was maintained at 40°. The stirring was continued for additional 8 hr, the resulting thick suspension was diluted with cold water (300 ml), filtered and washed free of acid. The solid was digested on steam bath for 0.5 hr with 10% sodium carbonate solution (100 ml), filtered and washed with water. Then it was extracted with 4% aqueous sodium bisulphite (200 ml), at the end of which sodium hydroxide was added and filtered. The operation was repeated 2-3 times and the combined filtrate was acidified at 80° with dilute hydrochloric acid (6N, 120 ml). The resulting bright yellow solid was filtered, washed with water until free from acid and dried (11.5 g). The crude quinone was crystallized from o-dichlorobenzene (50 ml) to give 9 g (37%), mp 258-260° (lit.[54] mp 259-260°).

Condensation of Acenaphthenequinone with o-Phenylenediamine: Preparation of the Azine 59

To a hot solution of acenaphthenequinone (0.206 g, 0.001 mol) in glacial acetic acid (8 ml) was added ethanolic solution of o-phenylenediamine (0.094 g, 0.001 mol, 5 ml). The precipitate which separated after 5 min. was collected, washed free of acid and dried to give 0.218 g (78%) of the azine 59, mp 239-240°.

Photolysis of Phenanthraquinonemonoimine (1)

Pure phenanthraquinonemonoimine (1) (0.823 g, 0.004 mol) in distilled dry THF (350 ml) was photolyzed under nitrogen atmosphere employing Hanovia high pressure 450 watt lamp and with a vycor filter. After irradiation for 8 hr, the solvent was removed under reduced pressure. TLC examination of the crude product did not show the presence of neither PQIA (7) nor the tetrabenzophenazine 13 .

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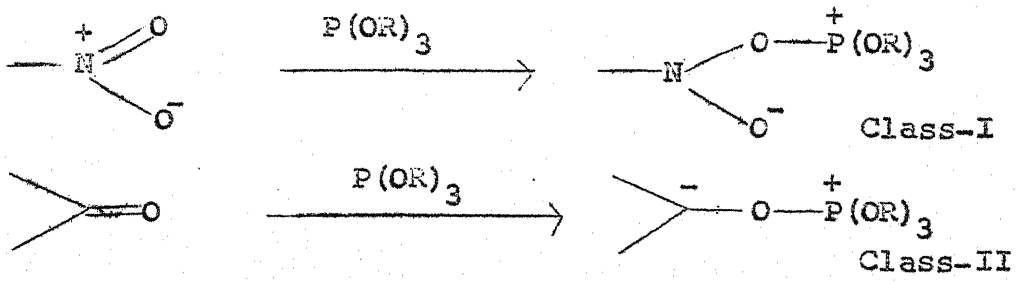
II. NEW FACETS IN THE UTILIZATION OF NUCLEOPHILIC SYSTEMS CREATED WITH TRIALKYLPHOSPHITES

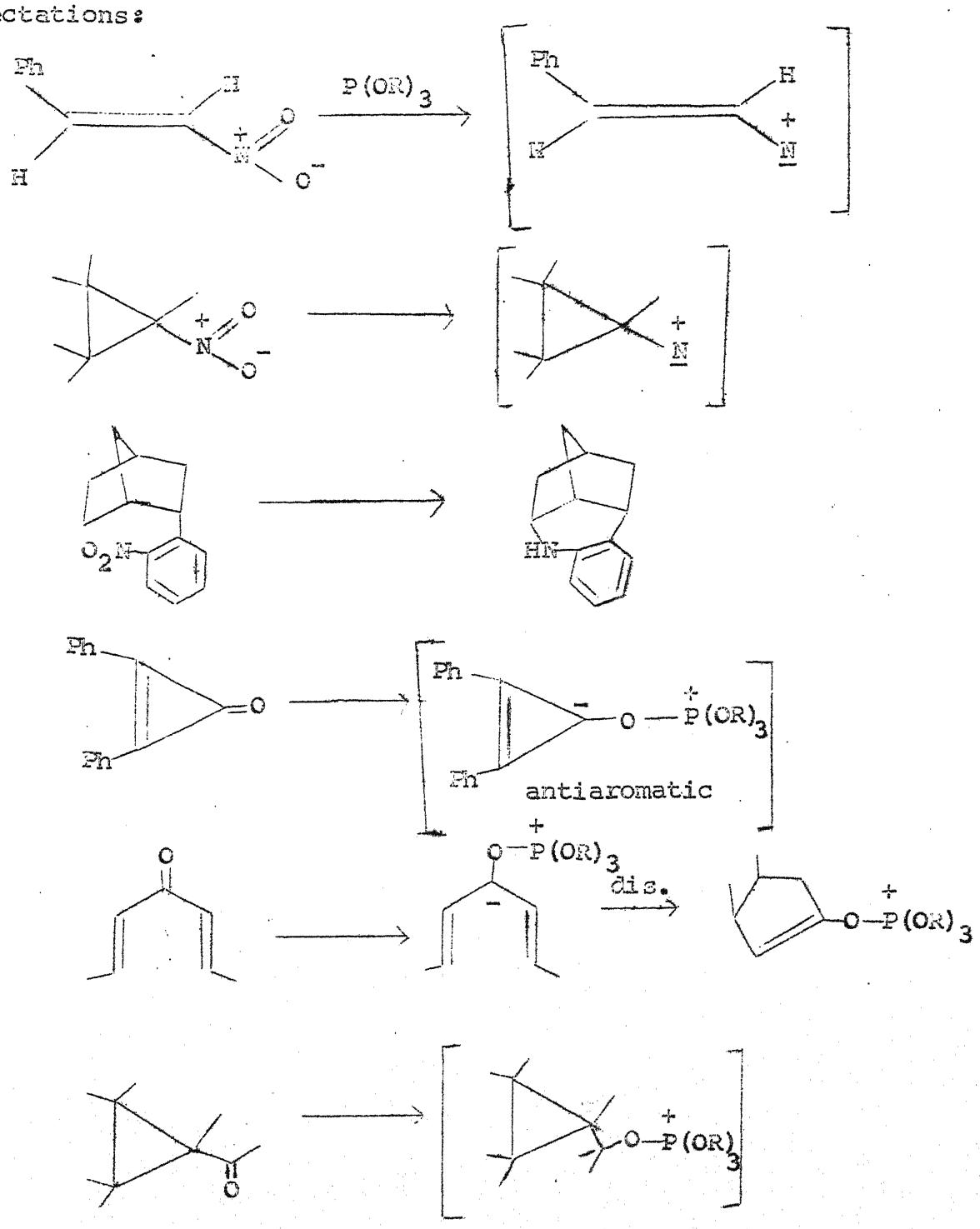
II.A INTRODUCTION

Trialkyl phosphites as reagents have captured the imagination of many in view of the great potentialities associated with these. The substrate employed practically involve every type of functional group combination and in recent years, from experience gained pertaining to the mode of their action, trialkylphosphites have been employed to bring about a specific change. This new approach comprising of planned application of the reagents would greatly enhance their practical utility and would provide simplified procedures for many transformations. The most fundamental property of these reagents is their ability to effectively interact with electrophilic substrates to create electron excess systems:



The present work is primarily concerned with the utilization of the electron excess system thus created to explore new possibilities in the area of synthesis and reaction mechanisms and

can be illustrated with some of the substrates on basis of the expectations:

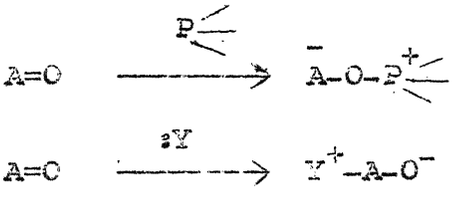


The results of these investigations are presented in II.C.

The vastness of data relating to interaction of trialkylphosphites with diverse substrates, particularly aromatic nitrocompounds, preclude inclusion of a detailed background pertaining to reactions involving these compounds. Fortunately several reviews and monographs on this topic are available.[1-9] Consequently only the most recent results are included in providing a proper background. Parenthetically whilst aromatic nitro systems have been extensively studied, those involving carbonyl functions have started receiving attention only in recent years.

II.B BACKGROUND

Much of the novelty associated with phosphorous (III) compounds is because of their great tendency to form bonds with oxygen thus creating electron excess on a less electronegative atom. This behaviour is to be contrasted with nucleophiles (:Y) wherein, in accordance with normal bond polarization, electron excess is created on the more electronegative oxygen:

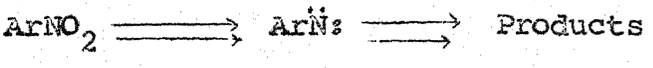


A = N,C

The further transformations of the initially formed dipolar adduct is very much a function of A and consequently this brief review is classified accordingly.

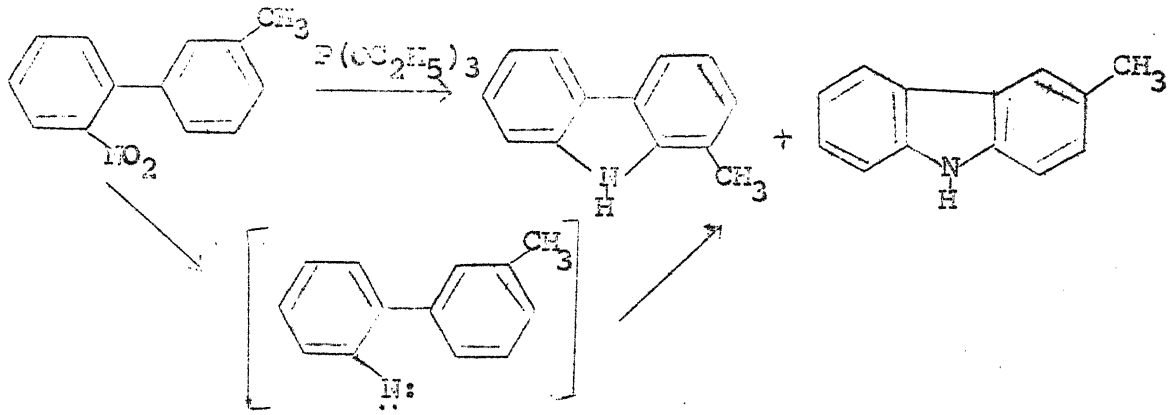
Reaction of Trialkyl Phosphites with Nitro and Nitroso Compounds

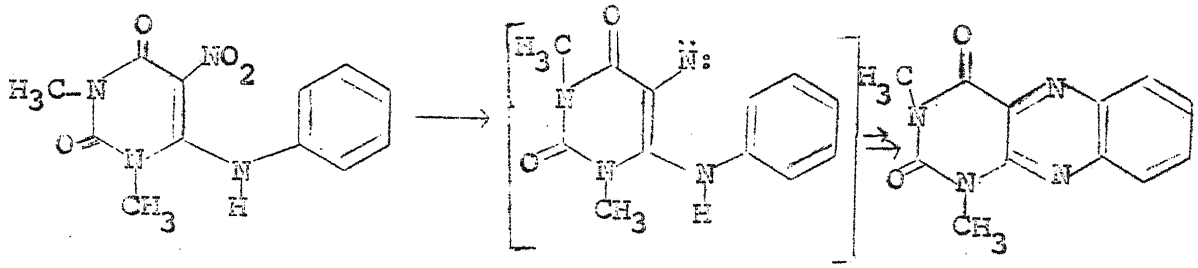
The formation of nitrene intermediate from aromatic nitro compounds is now accepted as a general reaction and much of the activity in this area since the last review[4] has been associated with the planned transformations of the expected nitrene intermediates:



C-H Insertion Reactions

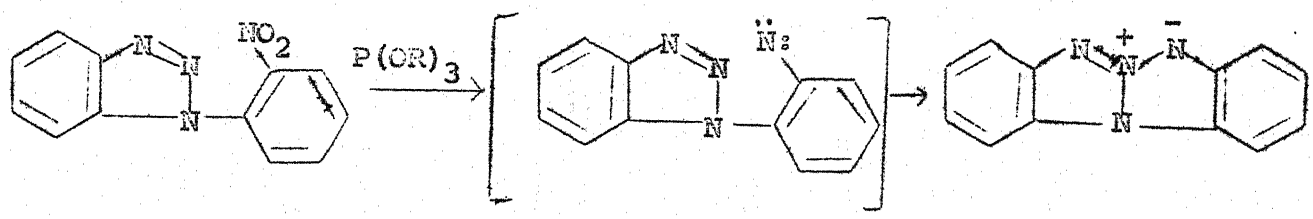
This well investigated procedure has given rise to a general route to diverse heterocyclic compounds and can be exemplified with two recent examples:[10,11]

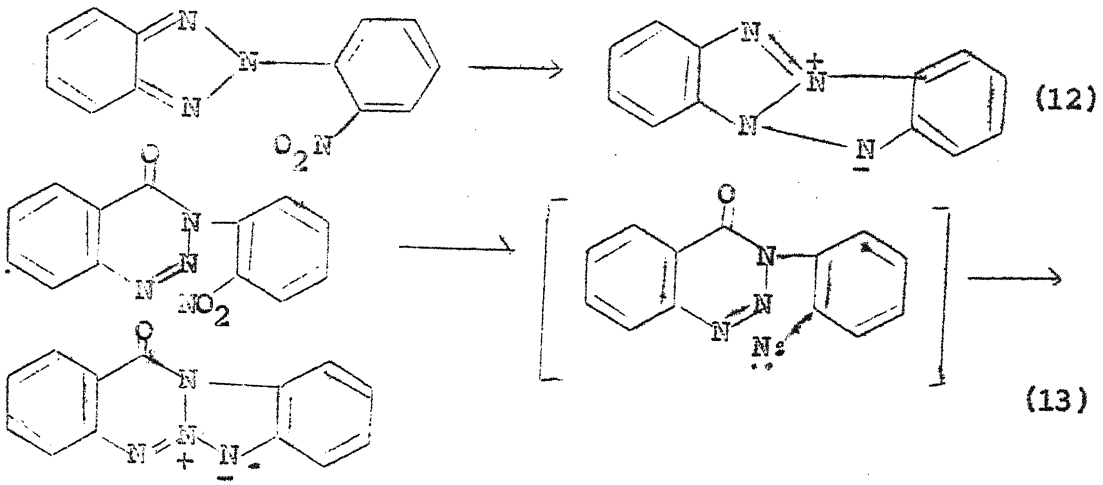




N-N-Bond Formation

Several mesoionic systems have been synthesized by neutralizing the electrophilic nitrene with nitrogen lone pairs:[12-15]





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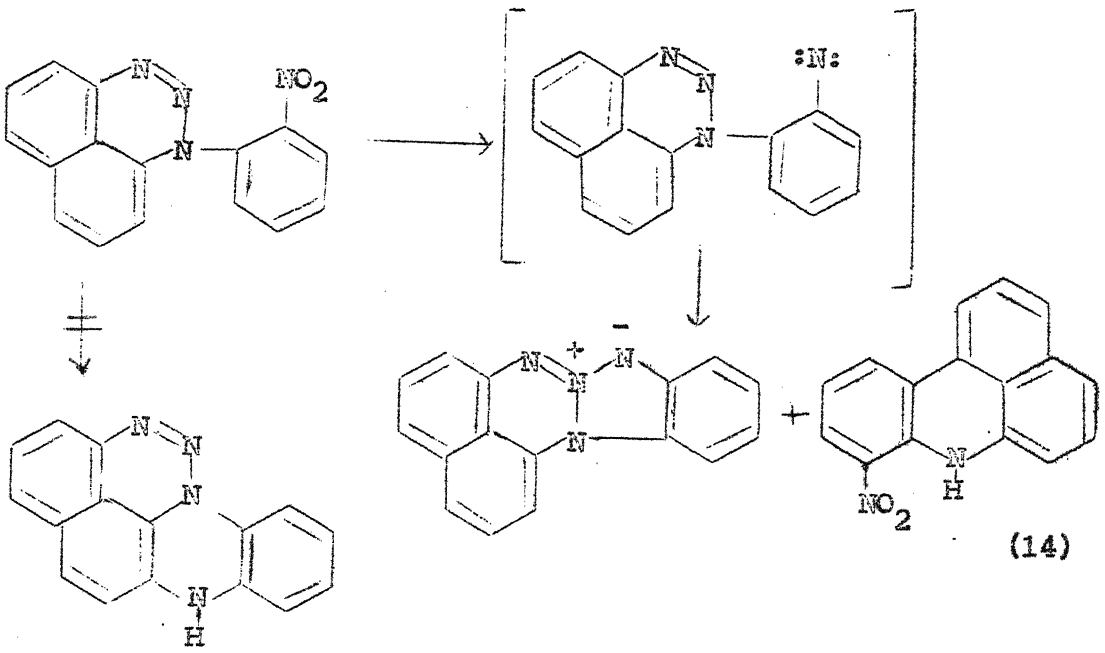

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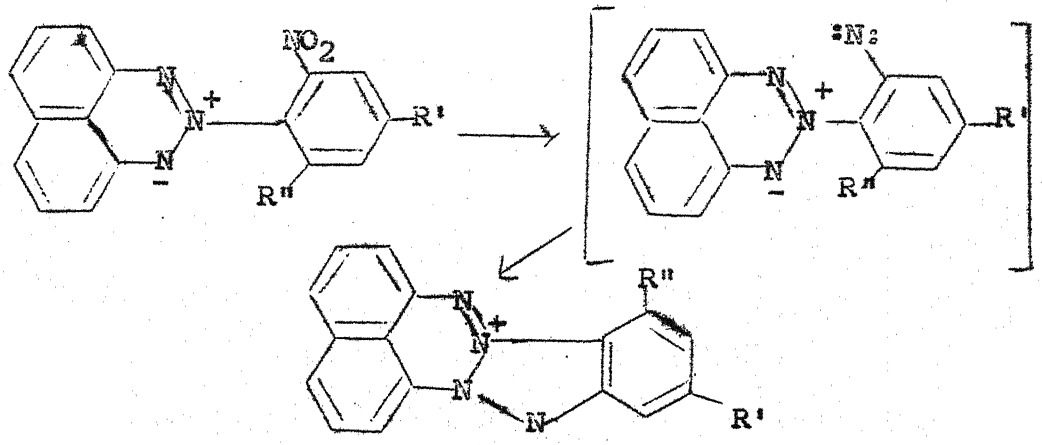
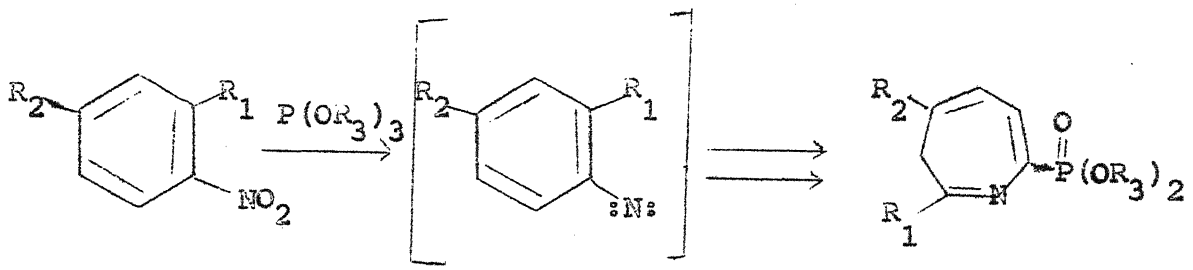
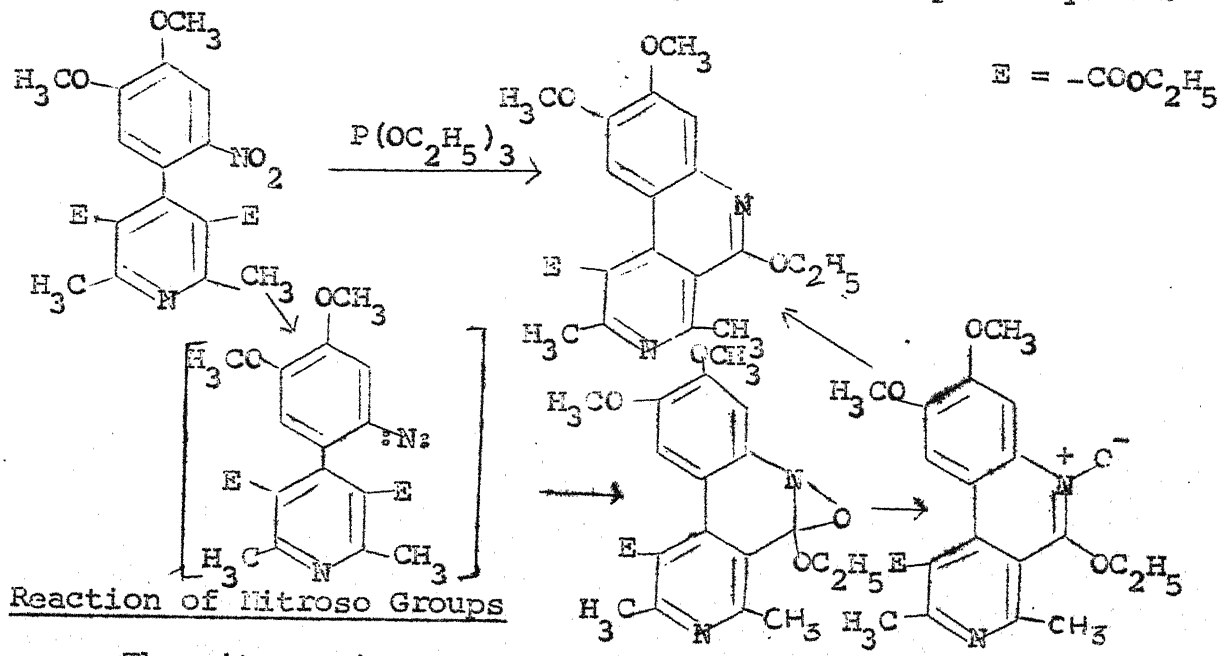


Cycloaddition Reaction

Aromatic nitrenes undergo cycloaddition to give bicyclic systems which are readily opened with trialkyl phosphites to give azepine derivatives.[16] This behaviour is analogous to phenylnitrene generated from the corresponding azide in presence of aniline:[17]



The nitrene could also undergo a (1+2) addition involving a transannular ester grouping leading to a heterocyclic system.[18]

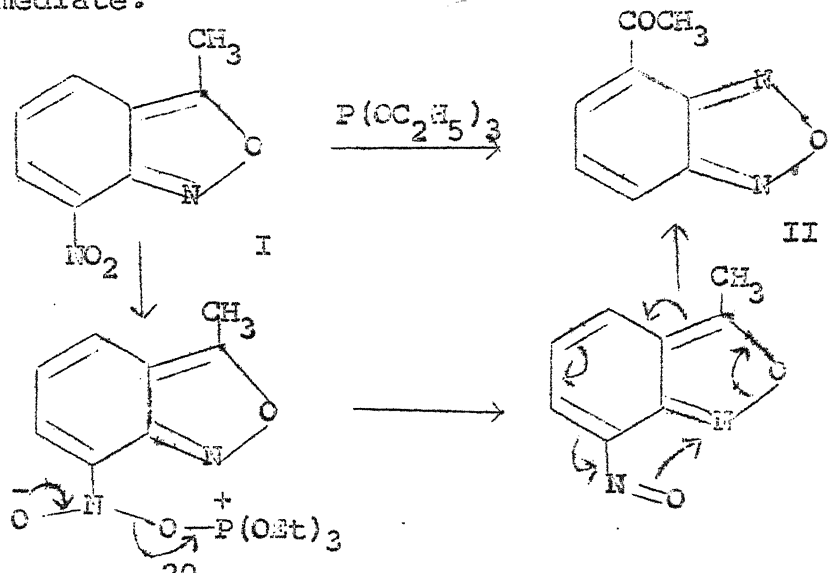


E = $-COOC_2H_5$

Reaction of Nitroso Groups

The nitroso intermediates involved in the above transformations could not be characterized as such because of the established higher reactivity of nitroso compounds towards trialkyl phosphites.

However, in the cases where possibilities for intramolecular reactions exist, compounds resulting from the nitroso intermediates arise. The fascinating I ⟶ II change involves an intramolecular cycloaddition through the initially formed nitroso intermediate:[19]

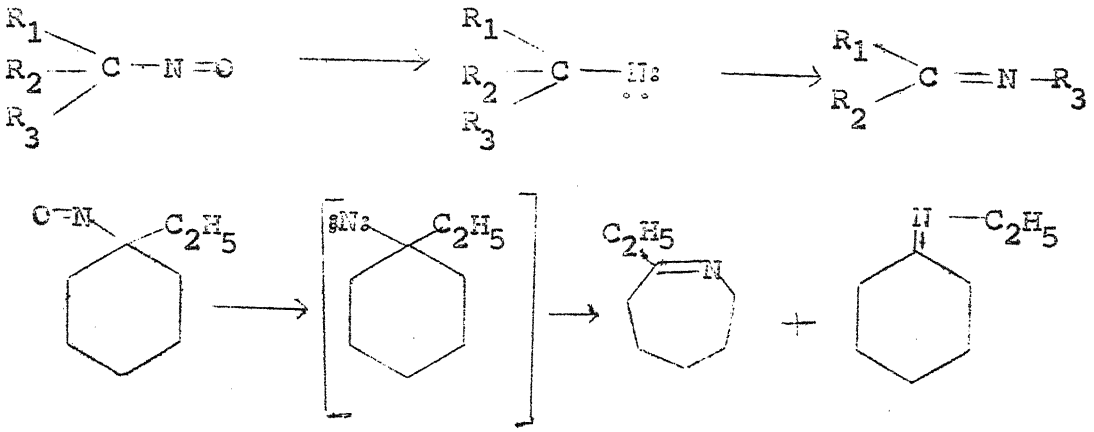


Recent studies[20] involving aromatic nitroso compounds leading to nitrene intermediates have shown the inconsequence of steric effects thereby supporting the initial O-P bond formation leading to dipolar intermediates:

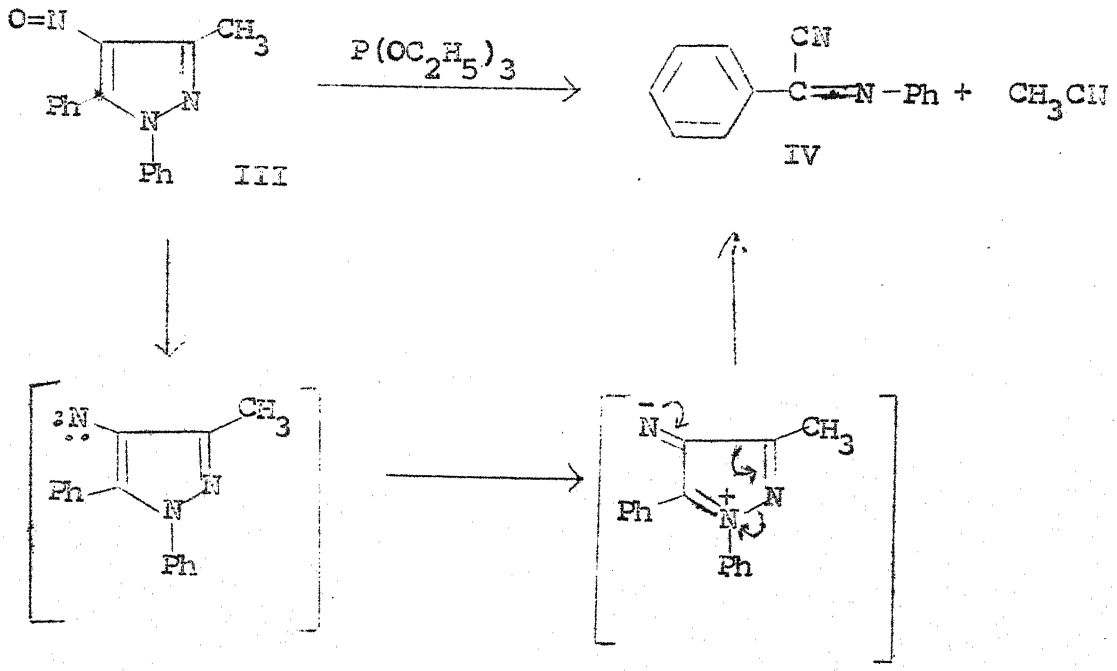
$$Ar\text{-}N{=}O \xrightarrow{P(OR)_3} Ar\text{-}\overset{-}{N}\text{-}O\text{-}\overset{+}{P}(OR)_3 \rightleftharpoons Ar\text{-}\ddot{N}\text{:} + \overset{O}{\overset{\|}{P}}(OR)_3$$

Very recently[21] it has been shown that tertiary nitroso compounds also undergo the expected deoxygenation with trialkyl phosphites to give the corresponding nitrenes which undergo alkyl migration

to give Schiff bases:

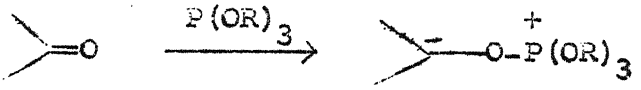


The III ⟶ IV change[22] involves an extensive fragmentation initiated by the nitrene intermediate:



Reaction of Trialkyl Phosphites with Carbonyl Compounds

The most versatile facet of the carbonyl group - trialkyl phosphite interaction is the formation of the dipolar adduct V which can open up diverse path ways depending on the nature of particular substrate:

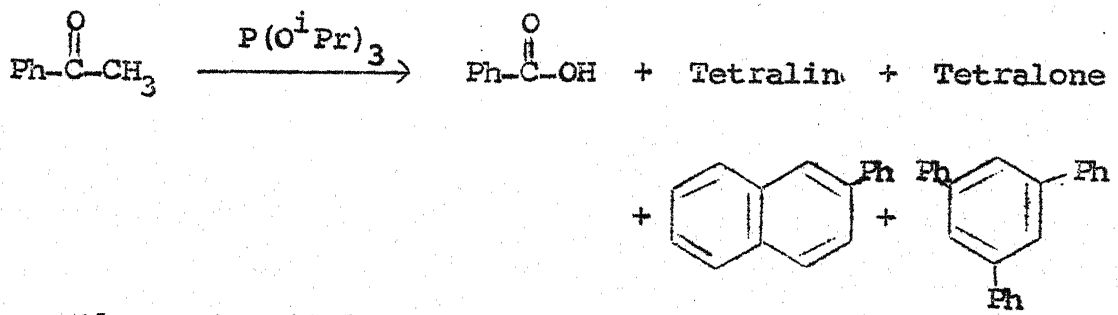


V

Several reviews and monographs pertaining to this aspect of P(III) chemistry are available[5-9] and consequently only those of either direct relevence or of recent origin are included.

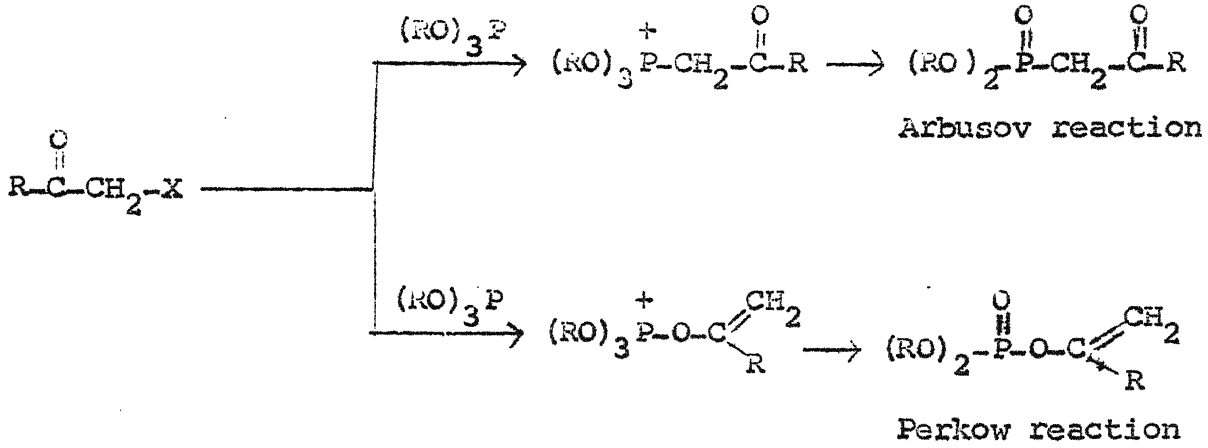
Reactions with Ketones

In general, only those carbonyl systems which can stabilize the dipolar adduct V react readily with trialkyl phosphites. Unactivated ketones undergo reaction only under forcing conditions to give complicated mixtures and the following example[23] illustrates this point:



Perhaps the most well known examples involving carbonyl systems

are the Arbusov[24] and the Perkow[25] reactions:

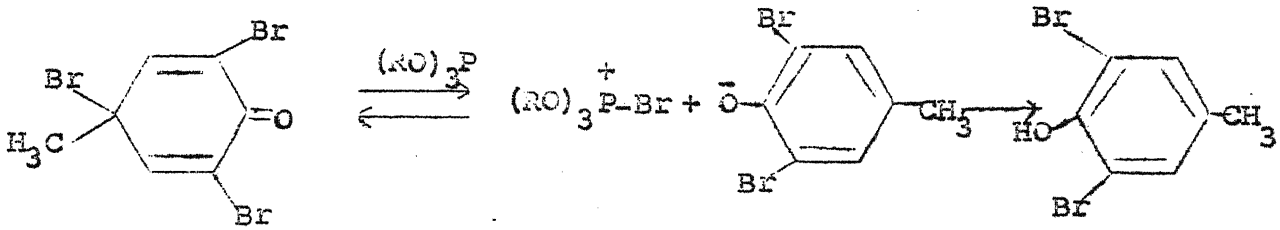


Arbusov reaction

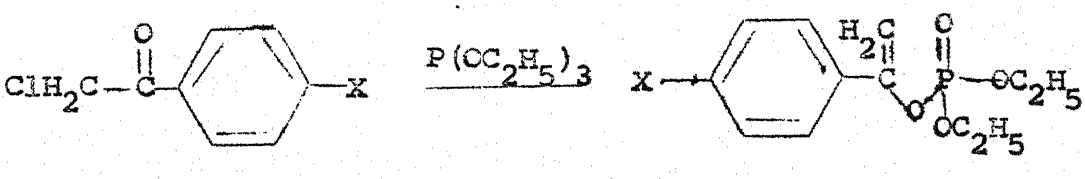
Perkow reaction

Several variants of these transformations have appeared in recent years.

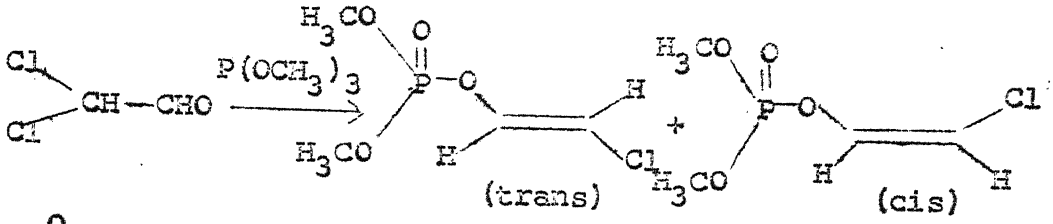
Arbusov Type[26]



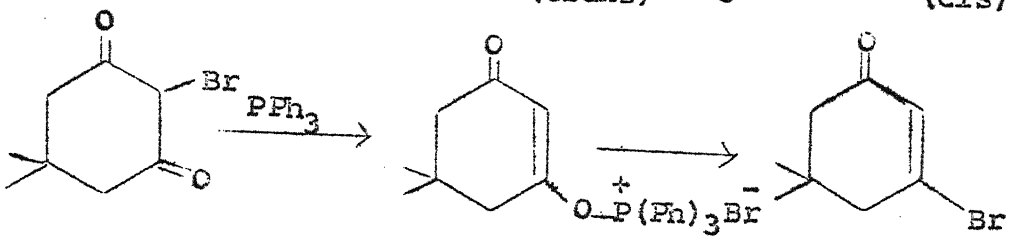
Perkow Type[27-30]



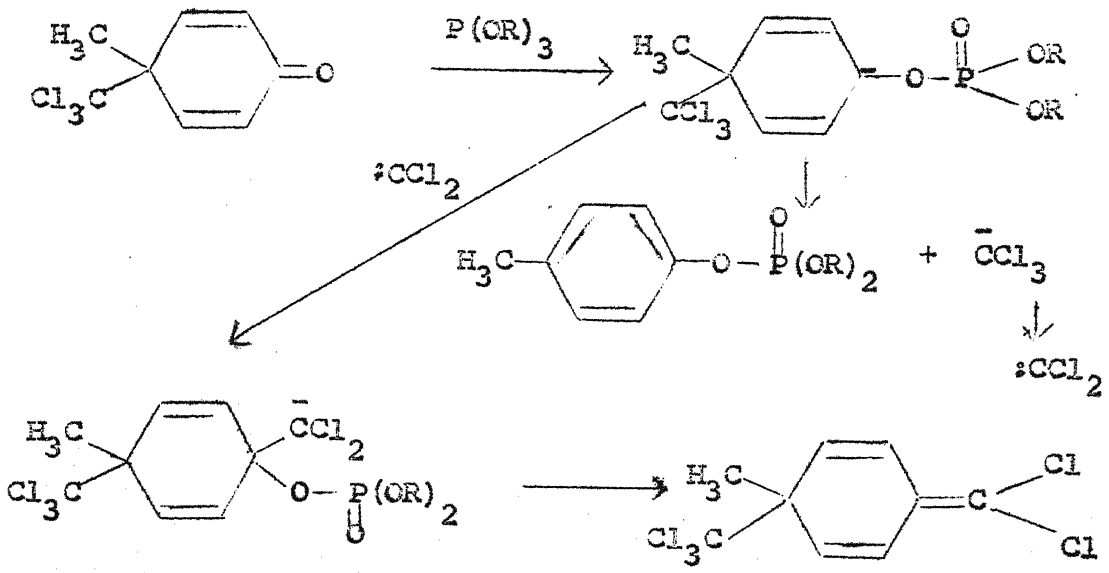
X = H, CH_3, OCH_3, Cl, NO_2



(28)



(29)

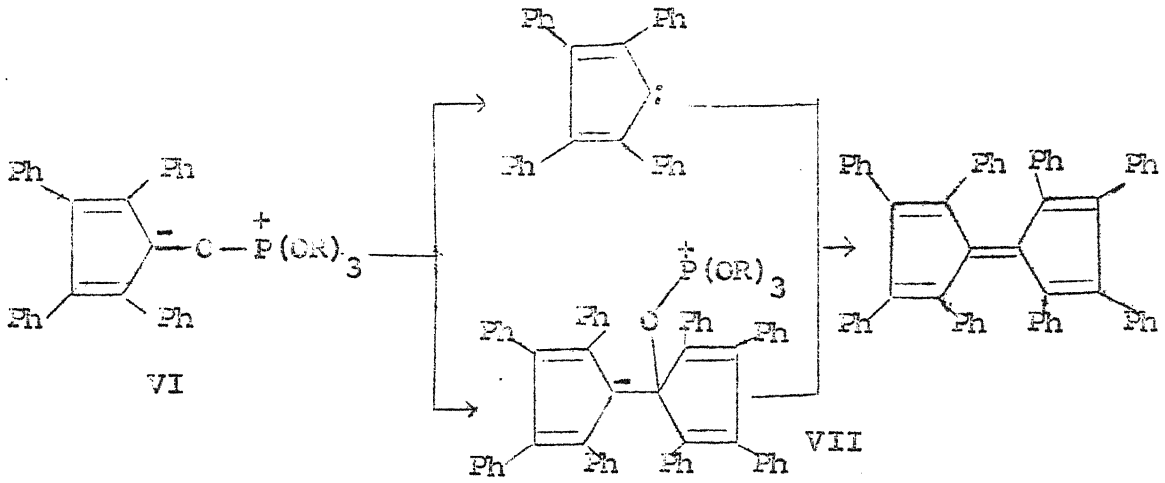


(30)

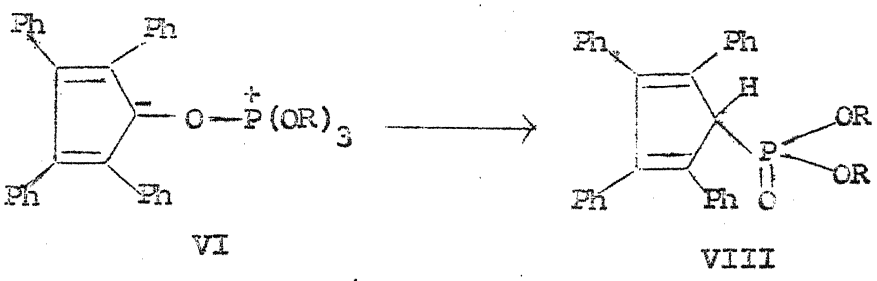
Reactions with Tetracyclone and Fluorenone

These systems, which can stabilize the electron excess created by participation in the aromatic (4n+2) π frame work, have been lately extensively studied. In the case of tetracyclone, much of the interest was because of the possibility of formation, from the initially formed dipolar species, either by direct

dimerization or through the intermediate carbene, the unknown octaphenyl fulvalene, a system expected to have a highly distorted middle π bond.

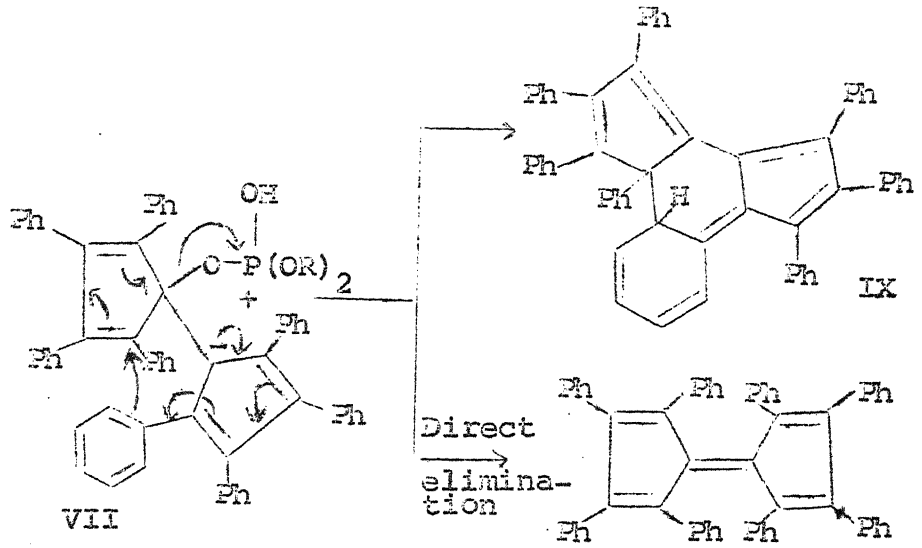


In the event the expected VI is produced quite readily[31,32] and is transformed to the phosphate ester VIII:[31]

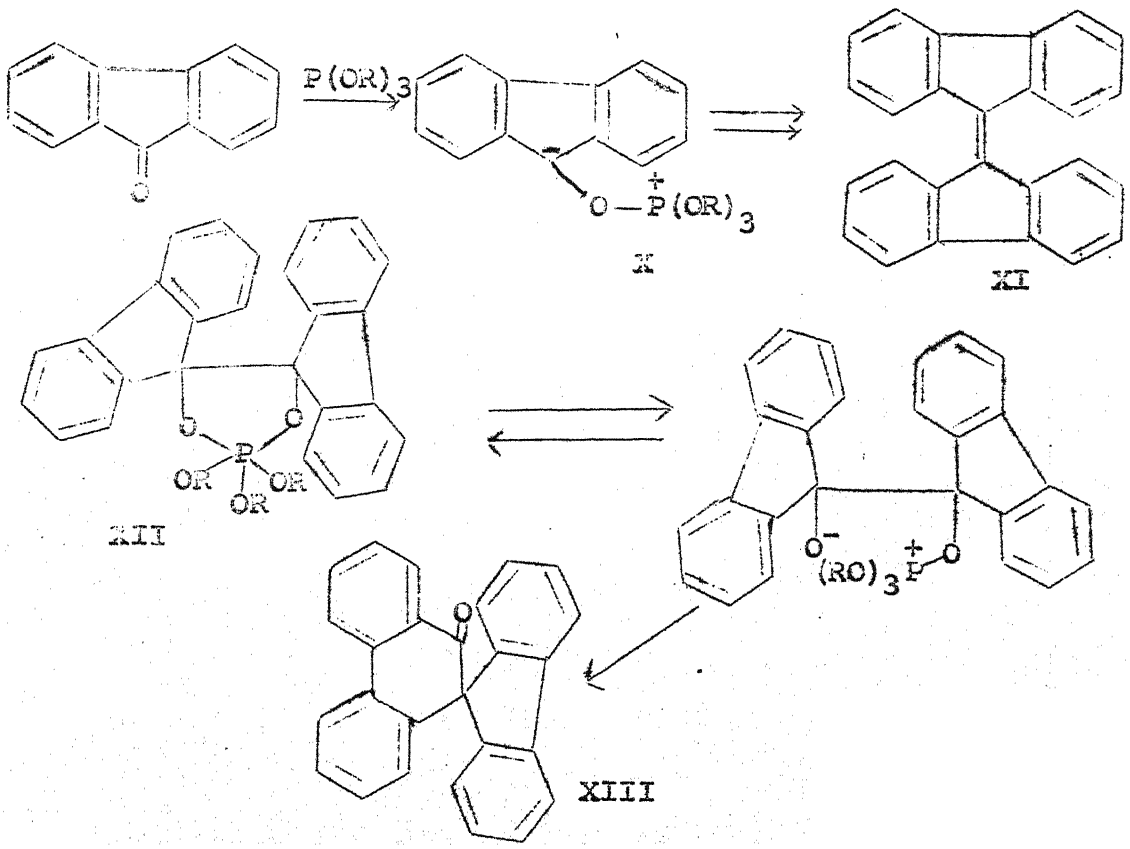


Interestingly compound VIII undergoes thermal dimerization involving elimination of elements of trialkyl phosphates from intermediate VII through one of the phenyl rings to give IX.[33]

Direct elimination would have yielded octaphenyl fulvalene!

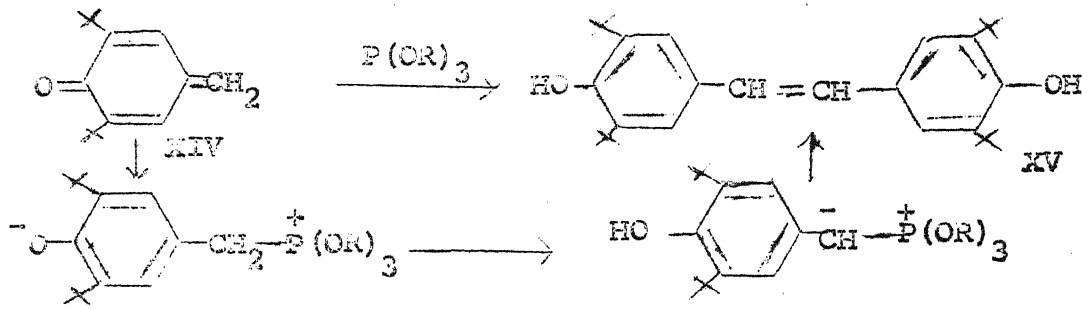


In the case of fluorenone the corresponding dipolar species X undergoes dimerization to give olefin XI and also adds to fluorenone to give cyclic phosphorane XII which in turn can be transformed to spiro system XIII:[34,35]

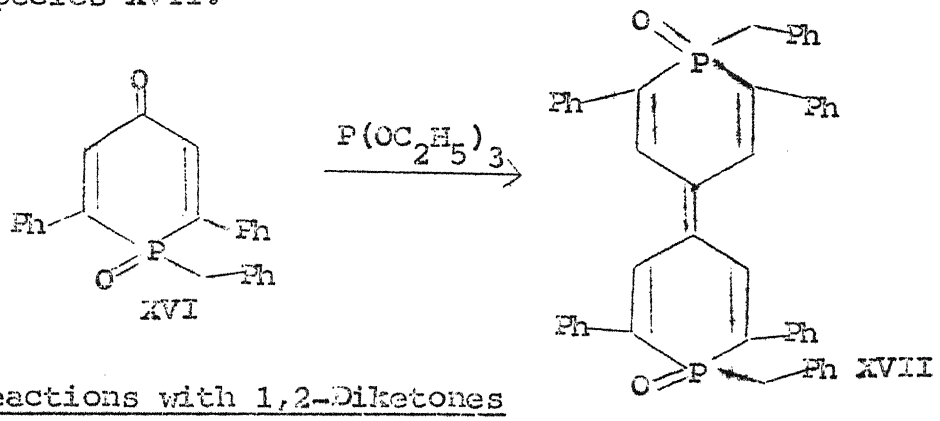


Crossed Conjugated Dienones

Compound XIV undergoes novel dimerization with $P(OEt)_3$ to give XV as major product:[36]

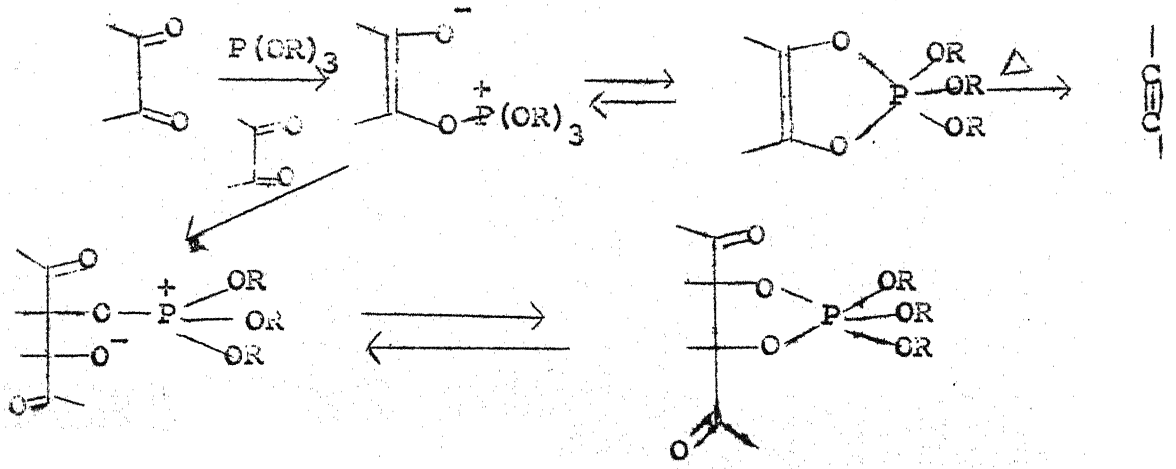


The phosphole XVI with trialkyl phosphite gives the dimeric species XVII:[37]



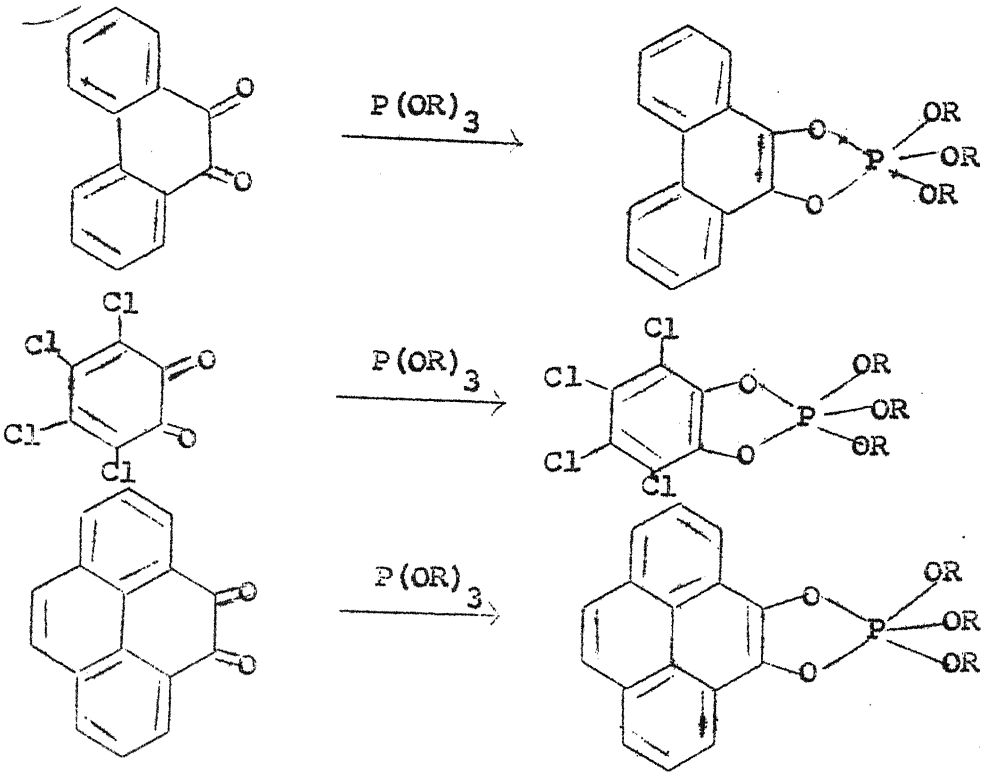
Reactions with 1,2-Diketones

Much of the interest in area of addition of trialkyl phosphites to carbonyl compounds was generated from studies of 1,2-diketones.[38] In these cases the electron excess system created is quite adequately stabilized by the adjacent carbonyl function. The most general features of this reaction are outlined:

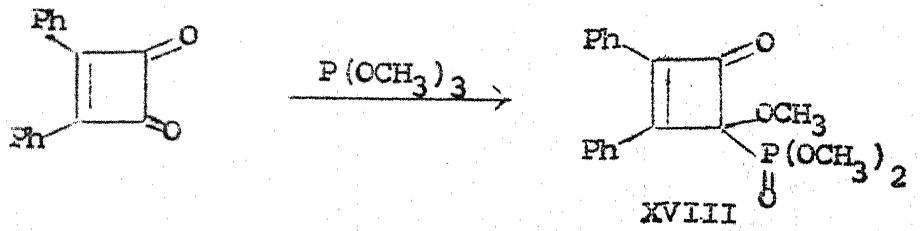


Recent studies of this reaction involving disubstituted benzils[39] have shown a ρ value of 1.86, thus indicating, as expected the creation of electron excess on the substrate in the transition state.

A variety of 1,2-diketones give the pentavalent oxyphosphoranes:

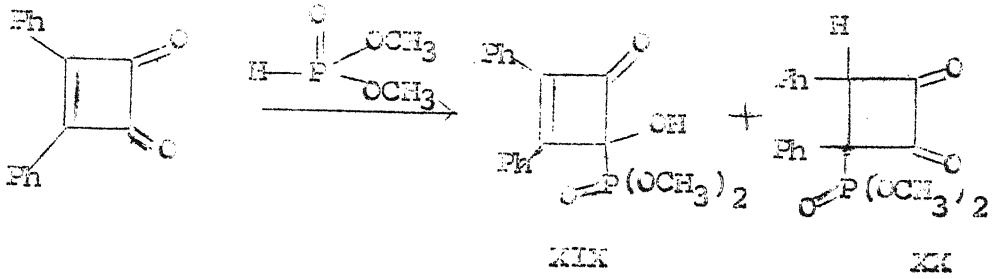


Recently[40] diphenyl cyclobutene 1,2-dione has been shown to react with trimethyl phosphite in a different fashion involving the formation of a C–P bond and leading to XVIII:



XVIII

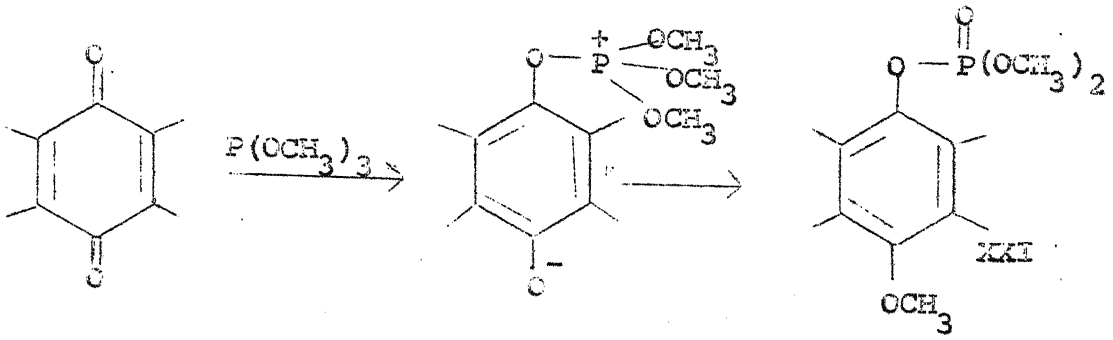
Similar C–P bond formation was found to take place with 1,2-diphenylcyclobutene-1,2-dione to give XIX and XX:



XIX XX

Reactions with 1,4-Diketones

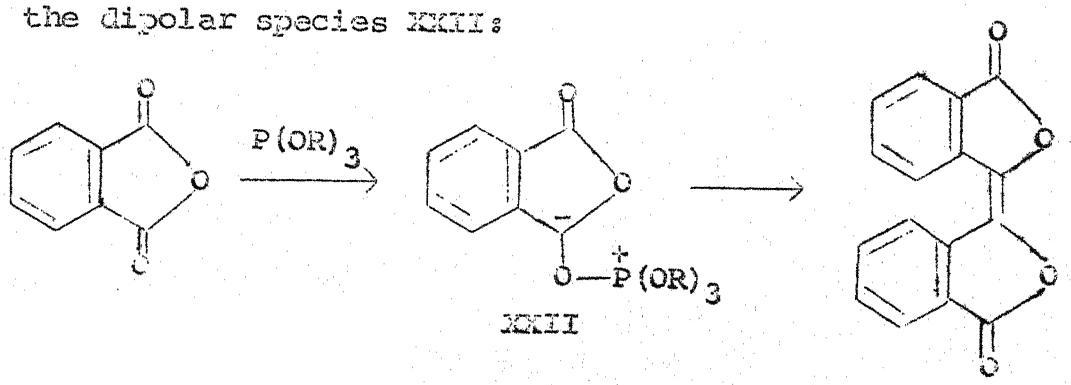
With 1,4-dicarbonyl compounds the initially formed dipolar species yield systems of the type XXI involving intermolecular group transfer:[41,42]



XXI

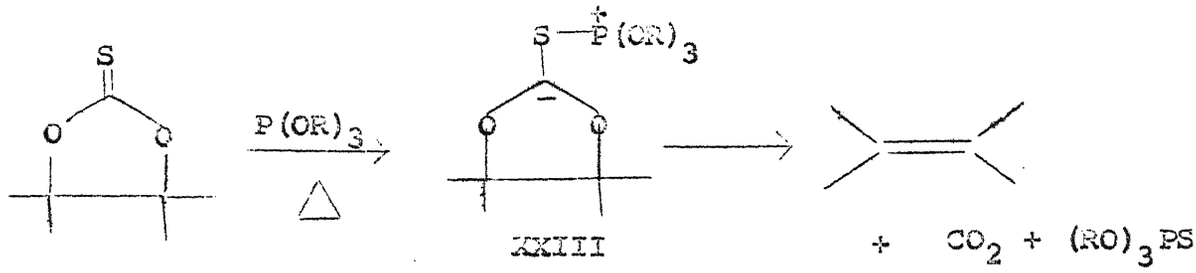
Reaction with Acid Derivatives

One of the earliest example[43] in this category is the reaction of phthalic anhydride leading to biphthalide involving the dipolar species XXII:

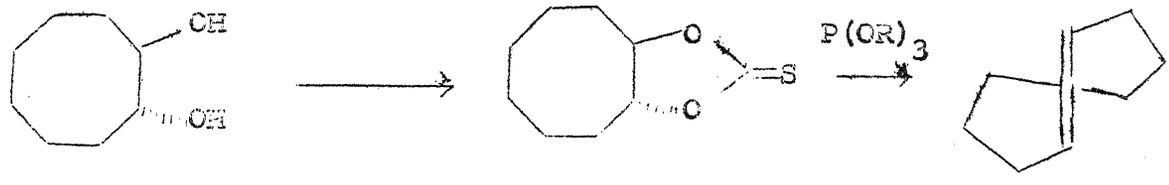


XXII

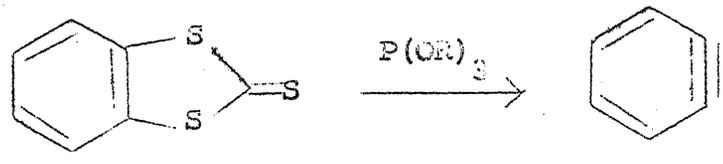
The highly stereospecific and practical Corey synthesis of olefins involves the fragmentation of dipolar species of type XXIII, generated from 1,3-oxalane-2-thiones, which in turn are readily prepared from the corresponding diols with thiophosgene:[44]



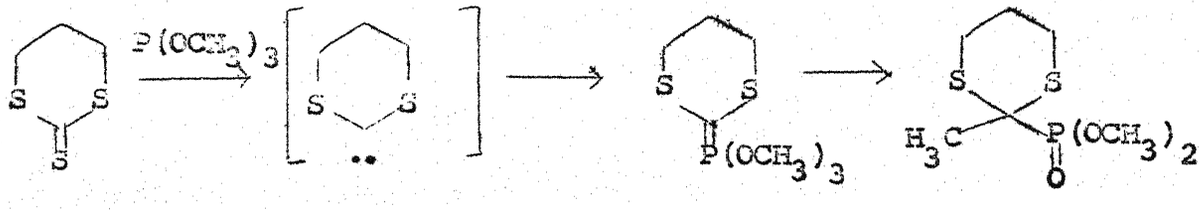
A variety of olefines have been prepared by this procedure and perhaps the most illustrative of this is the synthesis of trans-cyclooctene:[45]



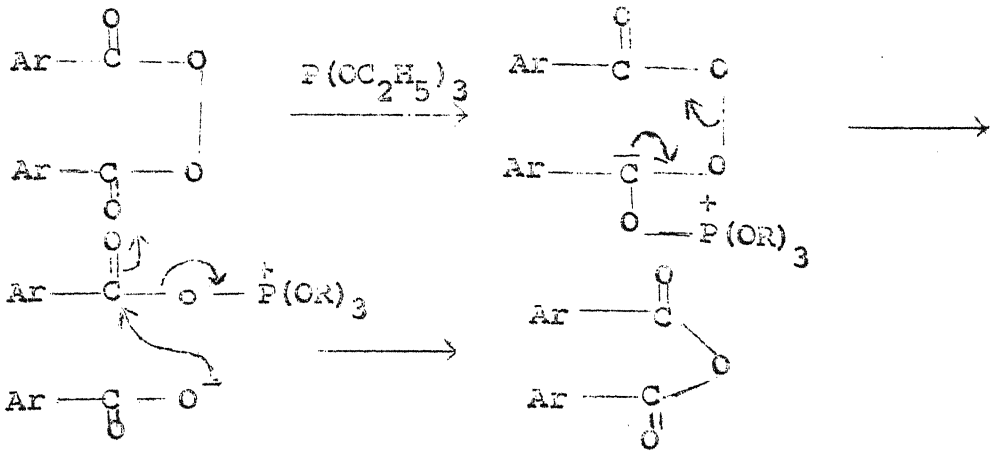
1,3-Dithialane-2-thiones can undergo similar reaction:[46]



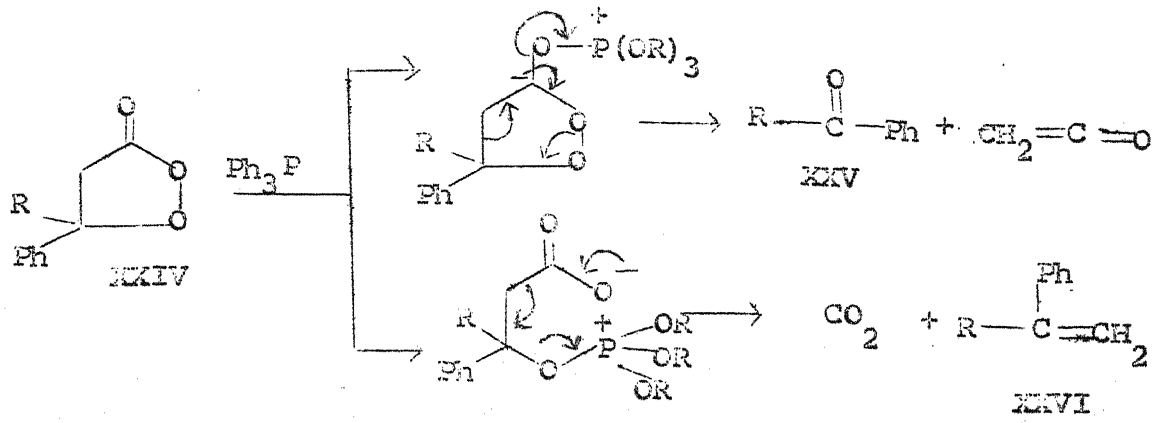
However, the reaction can not be used for the formation of sigma bonds:[47]



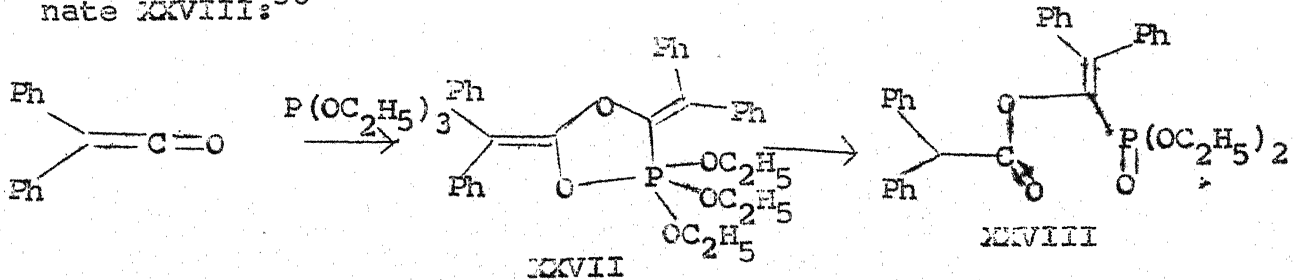
Diaroyl peroxides undergo loss of one oxygen to give the corresponding anhydrides:[48]



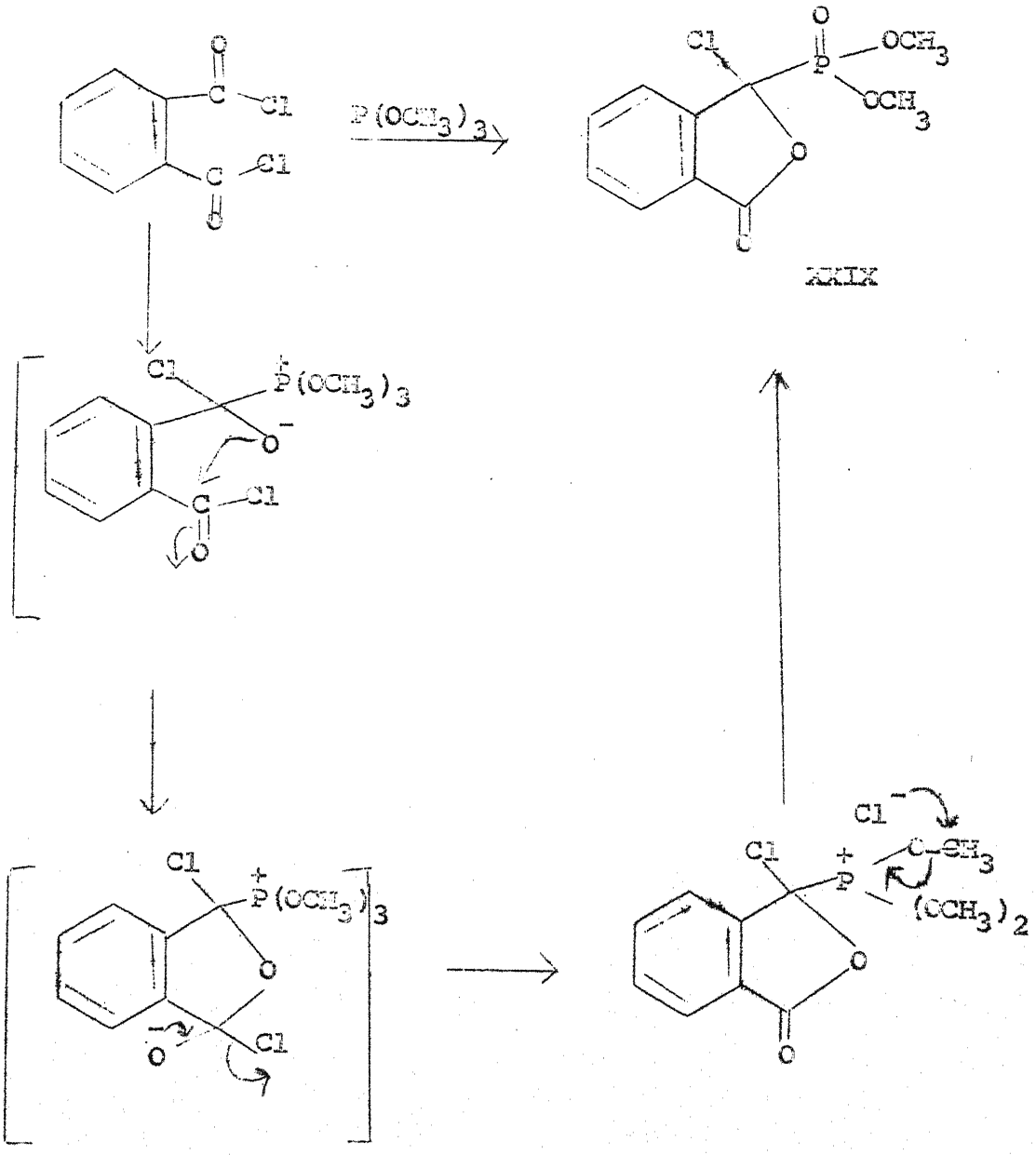
Similar pathway accounts for the fragmentation of the peroxy lactone XXIV to give XXV, XXVI, ketone and carbon dioxide:[49]



Diphenyl ketene undergoes dimerization to give oxyphosphorane XXVII which in turn is readily hydrolyzed to give the phosphonate XXVIII:[50]



Finally phthaloyl chloride by an intramolecular displacement reaction, gives the phosphonate XXIX.[51]



II.C PRESENT WORK

ABSTRACT

In connection with possible routes to the novel system, α,β-unsaturated nitroso, the trialkylphosphite deoxygenation of nitro compounds have been examined. β-Nitrostyrene reacts with trimethylphosphite in a highly exothermic manner to give phenyl acetyl dimethylphosphonate oxime. Triethyl and triisopropylphosphites also give similar products. Possible routes to the related nitroso cyclopropanes have been examined employing 2-nitro-spiro(cyclopropane-1,9'-fluorene) and 2-nitro-3-phenylspiro(cyclopropane-1,9'-fluorene). Whilst the former on reaction with triisopropylphosphite gave cyanomethylene fluorene, the later yielded the dimeric hydrocarbon 1,4-bisfluorenylidene-2,3-diphenylbutane. Structures of these novel transformation products have been established by analytical, synthetic and degradative procedures and their formation rationalized on basis of model studies.

Possible electrocyclic reactions of the pentadiene anion systems created from cross conjugated dienones and trialkyl phosphites have been investigated with the acyclic

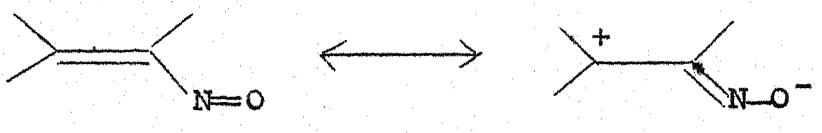
dibenzal acetone and the cyclic methandienone. Dibenzal acetone gave as the sole isolable product the unusual double Michael addition compound whose formation indicates the creation of the predicted pentadiene anion system. Remarkably the steroidal dienone with triethylphosphite at 145-150° underwent mere dehydration unaffecting the dienone system.

Unlike cyclopentadienones where the cyclopentadienide system can be created with trialkylphosphites, diphenyl cyclopropenone on reaction with triisopropylphosphite at room temperature gave no evidence for the anti-aromatic $4e^-$ cyclopropene anion; instead isopropyl α-phenyl cinnamate was isolated as the exclusive product.

The course of trialkylphosphite reactions with other substrates such as 3-bromophthalide are presented.

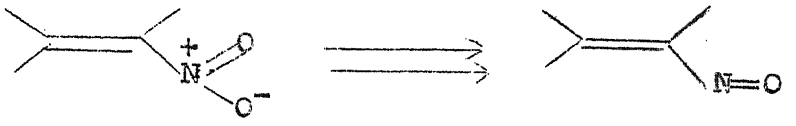
RESULTS AND DISCUSSION

System α,β-unsaturated nitroso has not been reported and work directed towards exploration of routes to this novel system, started in 1969, is continuing. Results gathered thus far, clearly indicates the importance of contributing structure 1a:



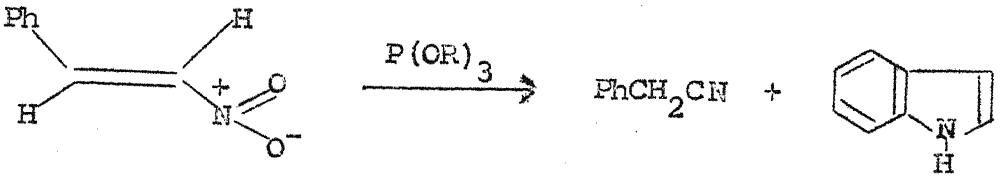
1 1a

An obvious route to 1 would be the controlled reduction of the easily available α,β-unsaturated nitro-system:



1

With this objective the reaction of β-nitrostyrene with trialkylphosphites was examined in some detail. In view of the tremendous information that is available relating to the reactions of diverse nitro functions, with $P(OR)_3$ (Section II.B), the nearly complete lack of information pertaining to β-nitrostyrene is indeed most surprising! From review to review this reaction is cited as a personal communication from Weinstock:[2,52]

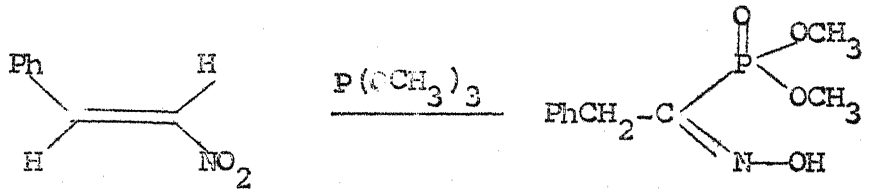


2 3 6% 2%

In the present work the reaction of $P(OCH_3)_3$, $P(OC_2H_5)_3$ and $P(OiC_3H_7)_3$ has been examined in detail and the following summarizes fragments of information gathered from innumerable experiments. It was found that the reaction —— under nitrogen — between one equivalent of 2 and 2 — 3 equivalents of $P(OR)_3$ became extremely vigorous after an induction period. With 10 m moles of 2 and 2-3 ml of $P(OCH_3)_3$ after an induction period

of 5 minutes, the inside temperature rose within 0.5 min to 185°! Infact, the temperature increase is so steep that the trialkylphosphite vapours that are produced are not condensed! Indeed, in preliminary experiments when the reaction vessel was connected to a gas collection unit through a condenser, the trialkylphosphite vapours collected. The exothermic reaction takes place even in presence of air as well as with samples of $P(OR)_3$ either freshly fractionated or that freshly distilled over sodium. In contrast, when either the reaction mixture was cooled or stirring was dispensed with, no reaction took place. All attempts to define an alterante set of conditions for the reaction have not succeeded.

The crude reaction mixture after removal of excess trialkylphosphite was found to be complex (TLC). With trimethylphosphite after careful chromatography, a crystalline compound was obtained to which structure 4 is given:



2 4

The yield of 4 is 20% and structural assignment is based on analysis and physical data.*

---

* 4, mp 138-39°.

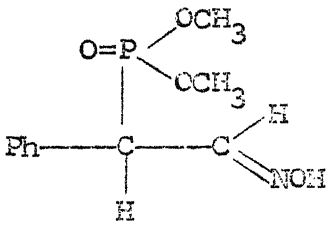
IR: ν_{max}(KBr) (cm^{-1}): 1220 (P=O), 1037 (P-O-CH_3), 1000, 925 and 840.

NMR: $\delta_{(CDCl_3)}$: 3.6 (d, J_{P-O-CH_3} = 11 Hz, 6 protons), 3.7 (d, $J_{P}\!\!\diagdown\!\!\diagup_{CH_2}$ = 20 Hz, 2 protons) and 7.4 (m, aromatic protons).

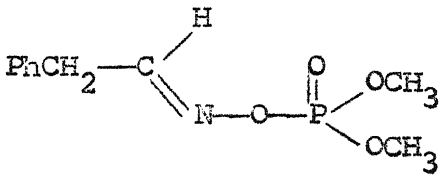
MS: m/e - 243.

TLC: Single spot R_f: 0.37 (Benzene:Ethyl acetate, 50:50).

The possible alternate structures 5 and 6 are ruled out on basis of NMR:



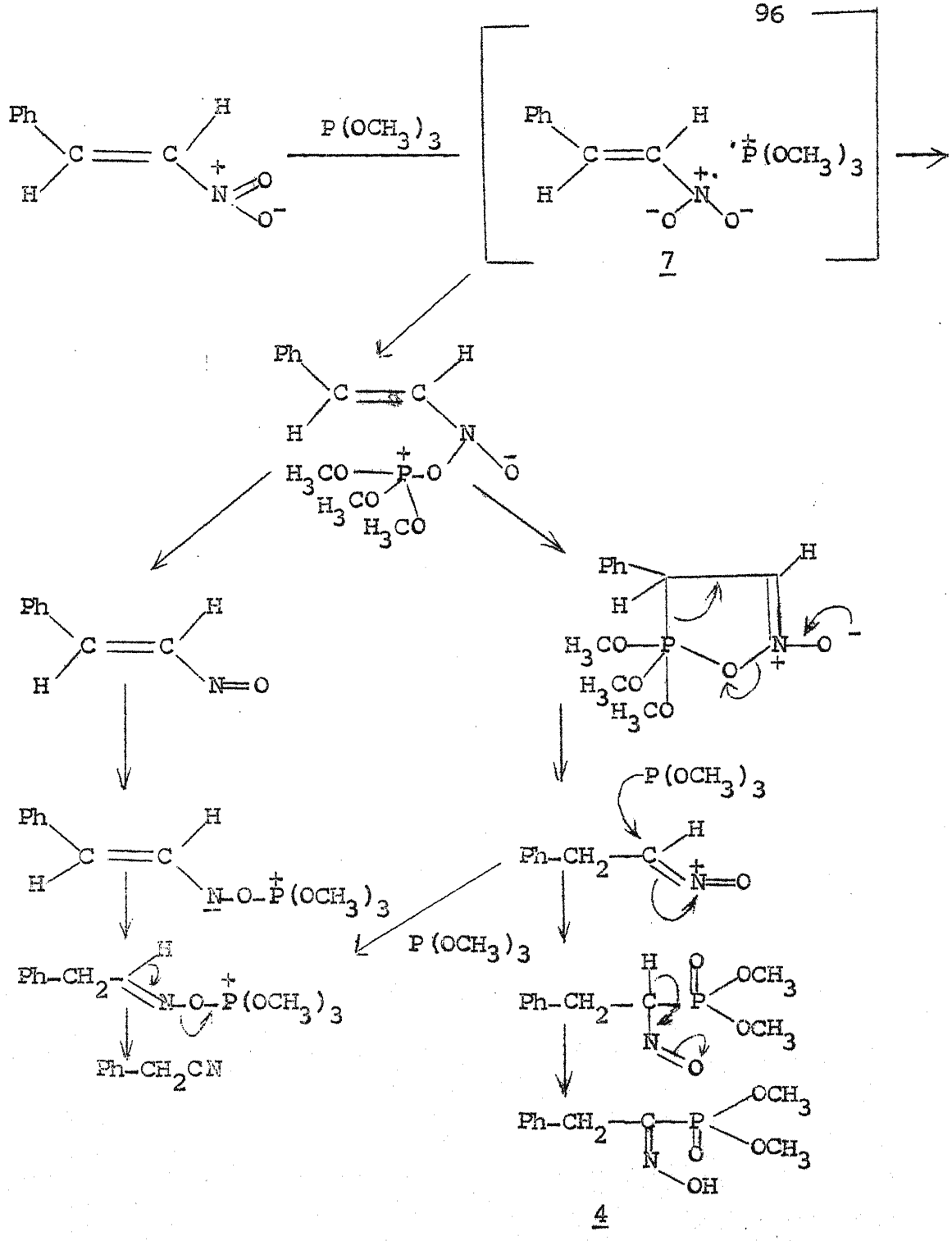
5



6

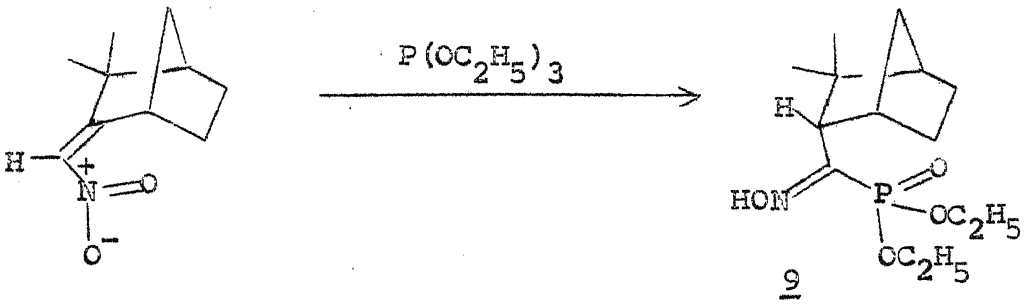
Further, the non-transformation to 2,4-DNP of phenylacetaldehyde as well as failure to form benzylcyanide on thermolysis are not in support of assignment 6.

The benzyl-cyanide claimed earlier[2,52] was confirmed by TLC. Attempts to characterize the remaining products were not fruitful. Reaction of 2 with triethylphosphite and triisopropylphosphite under similar conditions gave pure (TLC) viscous fractions corresponding to 4. The experimental observations suggest, the 1st step in the β-nitrostyrene-trimethylphosphite reaction is a thermal electron transfer to give intermediate 7 which then leads, by the exothermic process to adduct 8. A reasonable pathway for the 8 → 4 change as well as to benzylcyanide is presented below:



Preliminary attempts to identify 7 by esr have not succeeded. The reaction of α,β-unsaturated nitro compounds leading to products related to 4 appears to be general. ω-Nitrocomphene

was found to react with triethylphosphite under more vigorous condition to give a liquid product which is considered as 9 on basis of physical data.[53]

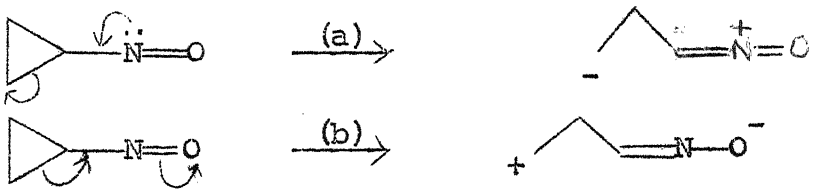


9

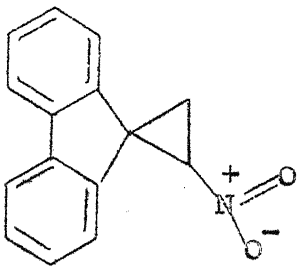
It is concluded that in the reaction of α,β-unsaturated nitro compounds with trialkylphosphites, the major pathway discerned thus far does not involve the α,β-unsaturated nitroso system.

In the deoxygenation reaction of nitro compounds with trialkyl-phosphites, nitrenes are the final products and it is recognized that the nitroso intermediate could be detected only in those cases where possibilities for intramolecular changes involving this function exist (Section II.B).

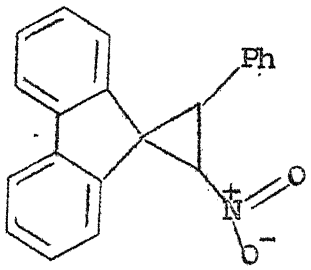
Such reasoning led to the novel nitroso cyclopropanes. In terms of reactivity these species were expected to behave either like cyclopropanols, showing tremendous tendency for ring rupture involving the nitrogen lone pair (a) or like α,β-unsaturated nitroso compounds, again leading to ring rupture in a complementary fashion (b):



The nitrocycloprpanes 10 and 11 were chosen since in these cases the tendency for the cyclopropane ring rupture through path (a) would be encouraged because of the fluorene system.

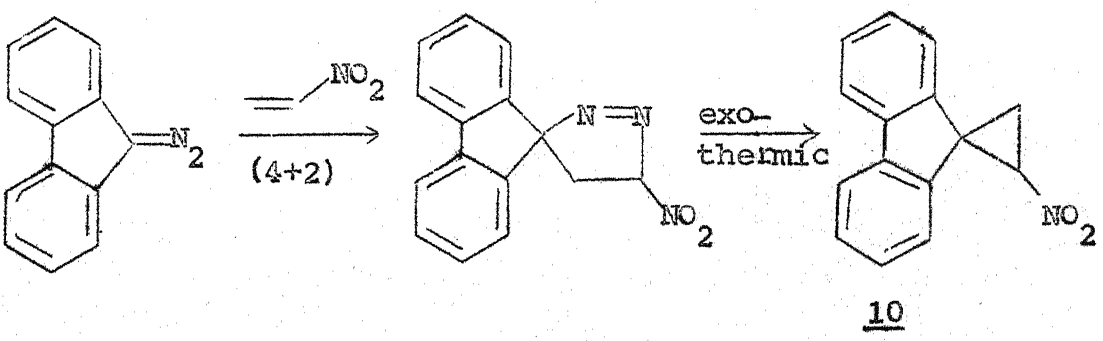


10



11

Compound 10 was prepared[54] by the reason of 9-diazofluorene with



10

nitro ethylene[55] and the proposed structure confirmed by

physical data.*

---

* 10 mp 110-111°.

IR : ν_{max} (KBr) (cm^{-1}) : 1531 (NO_2 asym.); 1351 (NO_2 sym.).

NMR: $\delta_{(CDCl_3)}$: 2.3 (q, anti-proton), 2.97 (q, syn.proton), 4.94 (q, t-proton) and 7.4 (m, aromatic protons).

TLC: Single spot R_f: 0.66 (Benzene:Ethyl acetate, 50:50).

Reaction of 10 with freshly distilled triisopropyl-phosphite under nitrogen gave after removal of excess reagent and chromatography, as the sole isolable product, the crystalline nitrile 12 in 40% yield. The structural assignment for 12 is supported by spectral** and analytical data as well as

---

** mp 108-108° (lit.[56] 110°).

IR : ν_{max} (KBr) (cm^{-1}) : 2203 (-C≡N) and 1600 (-C=C).

NMR: $\delta_{(CDCl_3)}$: 6.08 (s, olefinic proton) and 7.58 (m, aromatic protons).

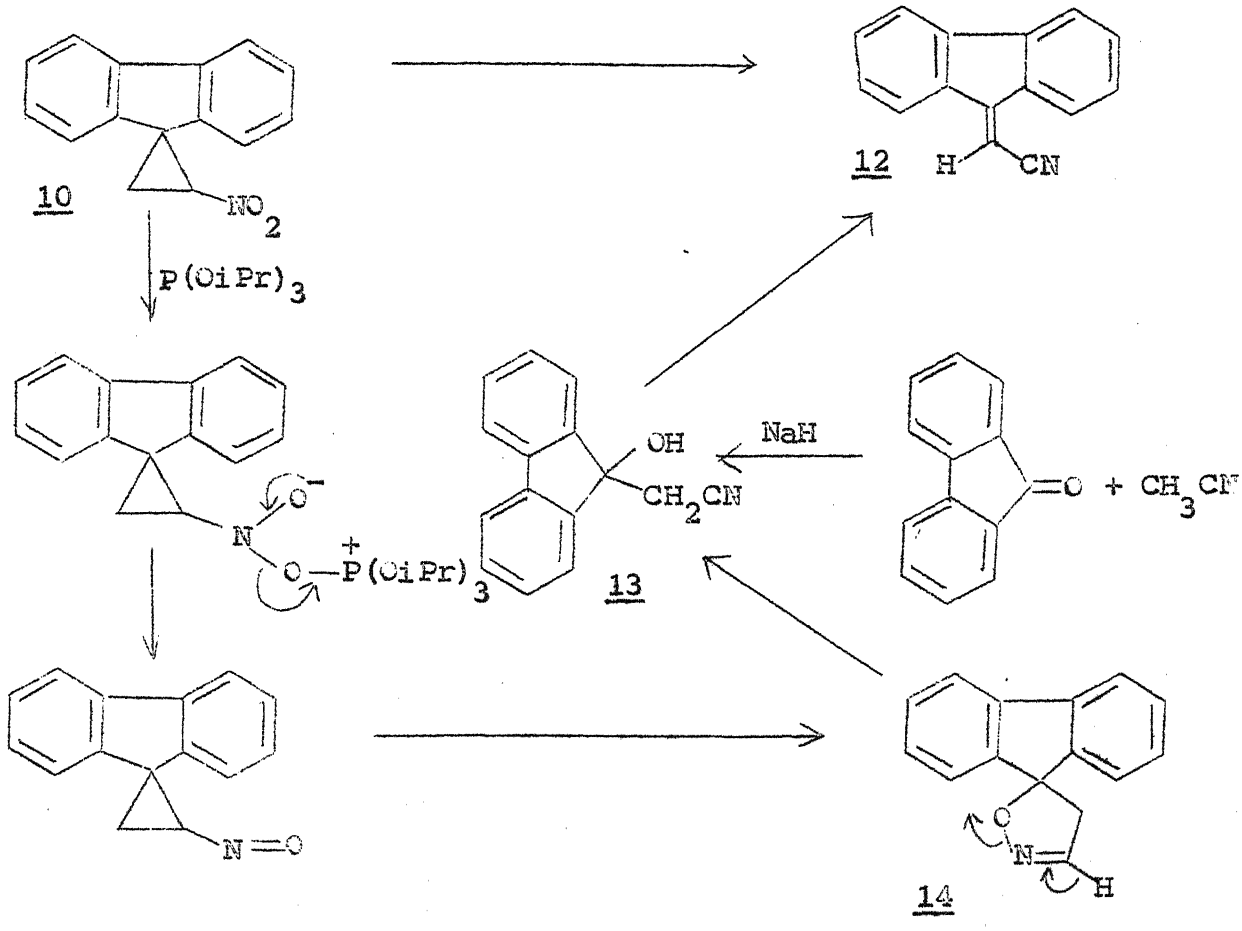
TLC: Single spot R_f: 0.75 (Ethyl acetate).

---

by comparison with authentic sample prepared by H_2SO_4-ACOH dehydration of alcohol 13, resulting from fluorenone - CH_3CN/NaH. Parenthetically, several attempts to prepare 12 from fluorenone acetonitrile-sodium hydroxide in ether as reported[56] failed.

The formation of 12 fulfils the expectations based on reactivity of nitroso cyclopropanes. The 10 → 12 change must

involve the expected rupture of the intermediate nitroso cyclopropane giving rise to the key isoxazoline intermediate 14. The 14 → 12 change is unexceptional and proceeds via - 13:



Parenthetically, the cyclopropane ring does enhance the reactivity of the nitro functions towards $P(OR)_3$ since unactivated nitro compounds generally do not react with these reagents.

2-Nitro-3-phenylspiro(cyclopropane-1,9'-fluorene), 11 on the other hand gave entirely different results!

Compound 11 was prepared[57] from 9-diazofluorene and β-nitro-styrene and the structural assignment confirmed with

physical data.*

---

* 11 mp 173-74° (lit.[57] 172°).

IR : ν_{max} (KBr) (cm^{-1}): 1538 (NO_2, asym), 1359 (NO_2, sym).

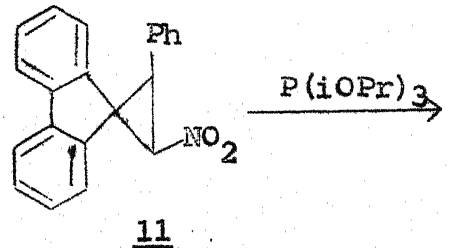
NMR: $\delta_{(CDCl_3)}$: 4.68 (d, J = 6 Hz; CH-Ph), 5.42 (d, J = 6 Hz; $CHNO_2$), 6.15 (d, J = 8 Hz; Heavily shielded fluorenyl 8-proton) and 7.4 (m, aromatic protons).

MS : m/e - 313.

TLC: Single spot R_f: 0.70 (Benzene:Ethyl acetate, 50:50).

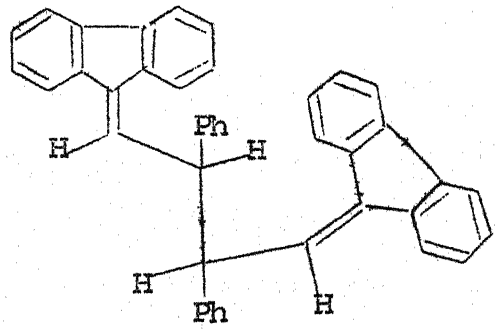
The NMR spectrum of 11 is noteworthy because of the presence of the doublet at 6.15 ppm (J = 8 Hz) due to heavily shielded aromatic proton. This unexpected development made it necessary to examine the NMR of several related systems. The results and their utility in defining the conformations of systems related to 11 are presented in appendix.

Reaction of 11 with triisopropyl-phosphite under conditions of the 10 → 12 change gave as the sole isolable product a nitrogen free product which was subsequently identified as the dimeric hydrocarbon 15:



11

P(iOPr)3



15

The yield of 15 was 42% and to our knowledge this is the first example of complete removal of elements of nitro group with trivalent phosphorous. Unexpectedly the structural elucidation of 15 was beset with unusual difficulties. The NMR spectrum showed besides aromatic and olefinic protons the presence of a doublet of triplets centred around 5.1 in the ratio of 1:2:1 equivalent to 2 protons. This fact combined with analytical results suggested dimeric structure 15 where in the benzylic protons are non-equivalent and a coincidence of chemical shift and coupling constant gives rise to the unusual triplet pattern. The latter assumption was verified by having the NMR recorded in a 250 MHz instrument.* As expected the enhanced chemical shift

---

* 15 mp 230-231°

IR : ν_{max} (KBr) (cm^{-1}) : 1639, 1592, 1486 and 1435.

NMR: δ_{CDCl_3} (60 MHz) : 5.1 (d,t,2-benzilic protons) and 7.3 (m, aromatic protons).

NMR: δ_{CDCl_3} (250 MHz) : 5.12 (J = 7 and 2 Hz) and 4.98 (J = 7, and 2 Hz).

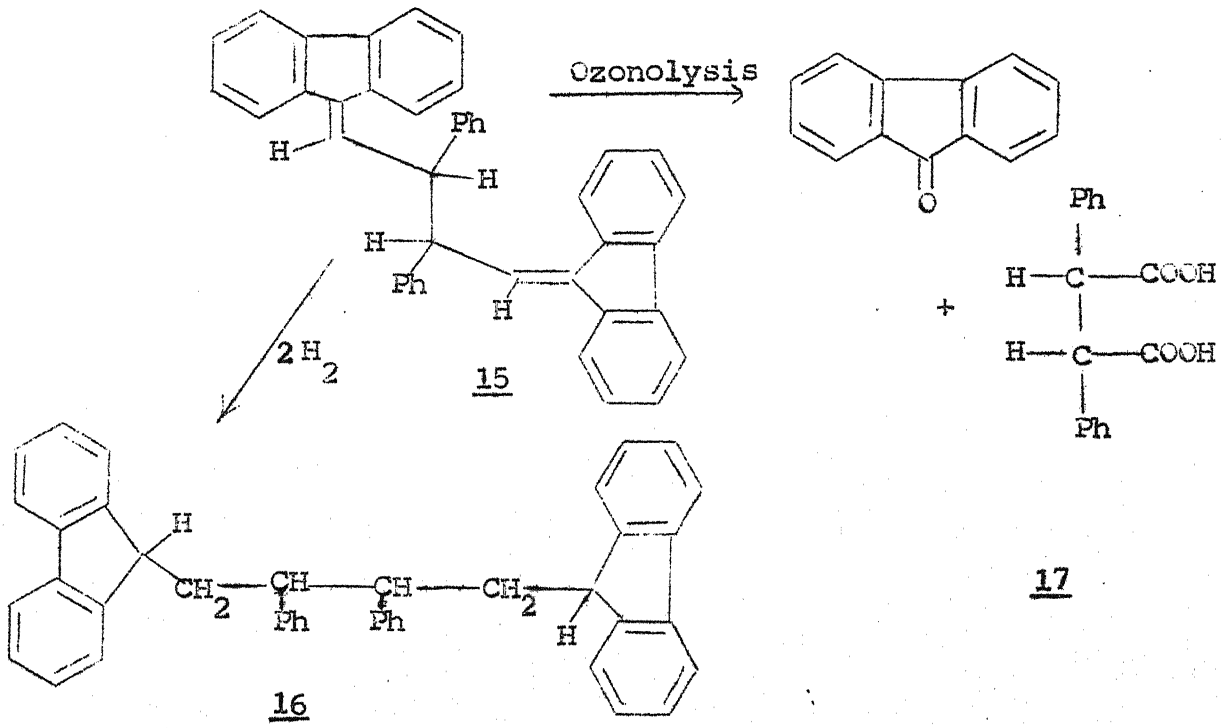
TLC: Single spot R_f : 0.75 (Benzene:Ethyl acetate, 50:50).

---

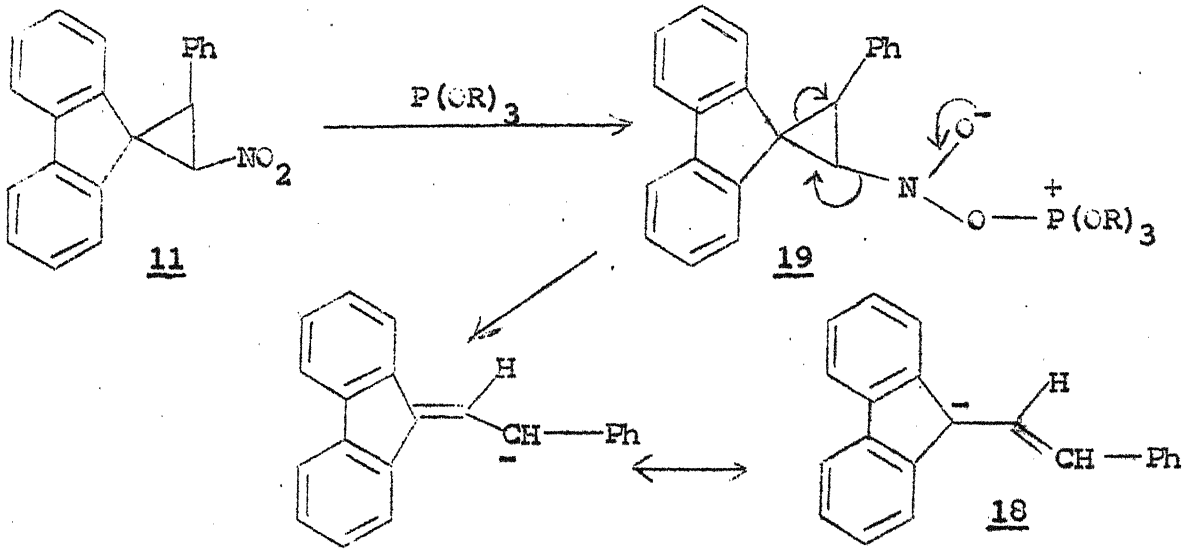
separation caused the benzilic protons to appear as a doublet of quartets. Interestingly the mass spectrum recorded at 260° exhibited only peaks corresponding to the monomeric unit. However, the molecular weight by osmometric method (540) was in good agreement with the dimeric structure (534).

Compound 15 readily consumed two moles of hydrogen to give tetrahydro derivative 16. The structural assignment for 16 is supported by spectral and analytical data. Interestingly unlike 15 the mass spectrum of 16 had the expected m/e peak at 538.

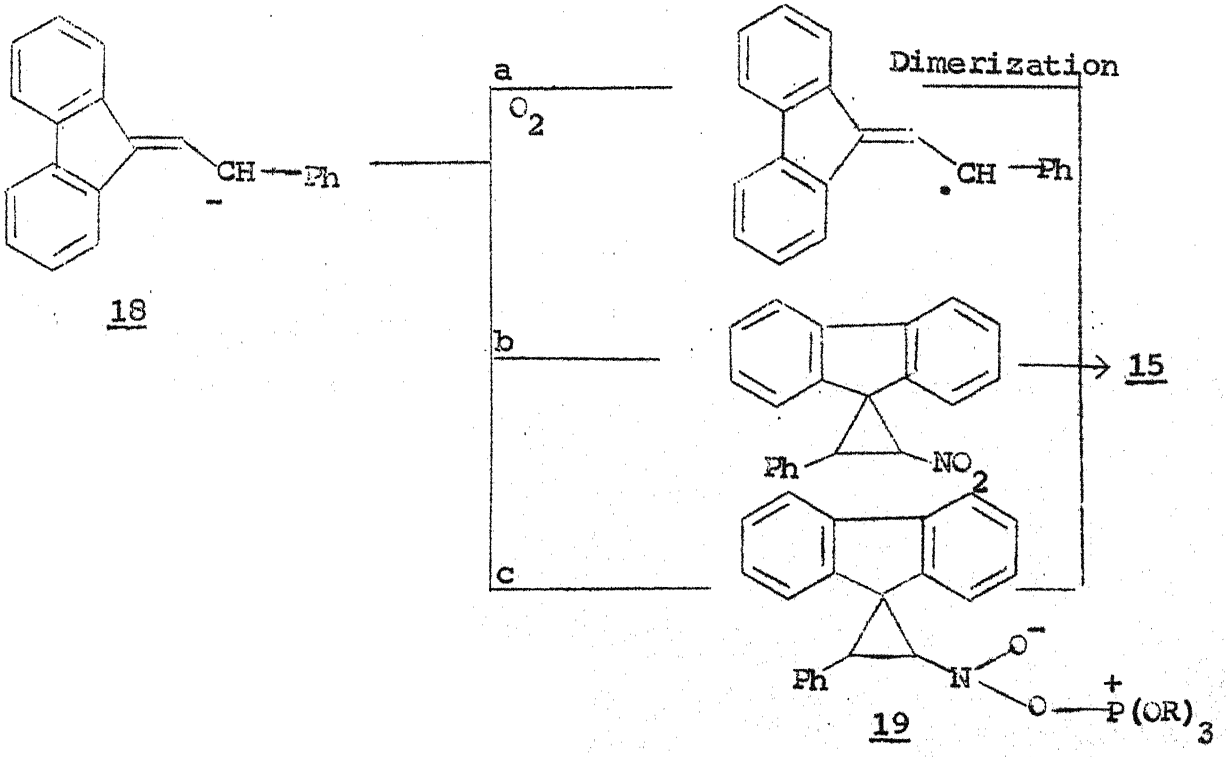
Ozonolysis of 15 involving an oxidative work-up gave fluorenone and meso-diphenyl succinic acid 17. The structure of the ozonolysis product 17 was confirmed by comparison with authentic sample prepared[58] by hydrolysis of meso-diphenyl succinonitrile, which in turn was made[59] starting from benzyl cyanide:



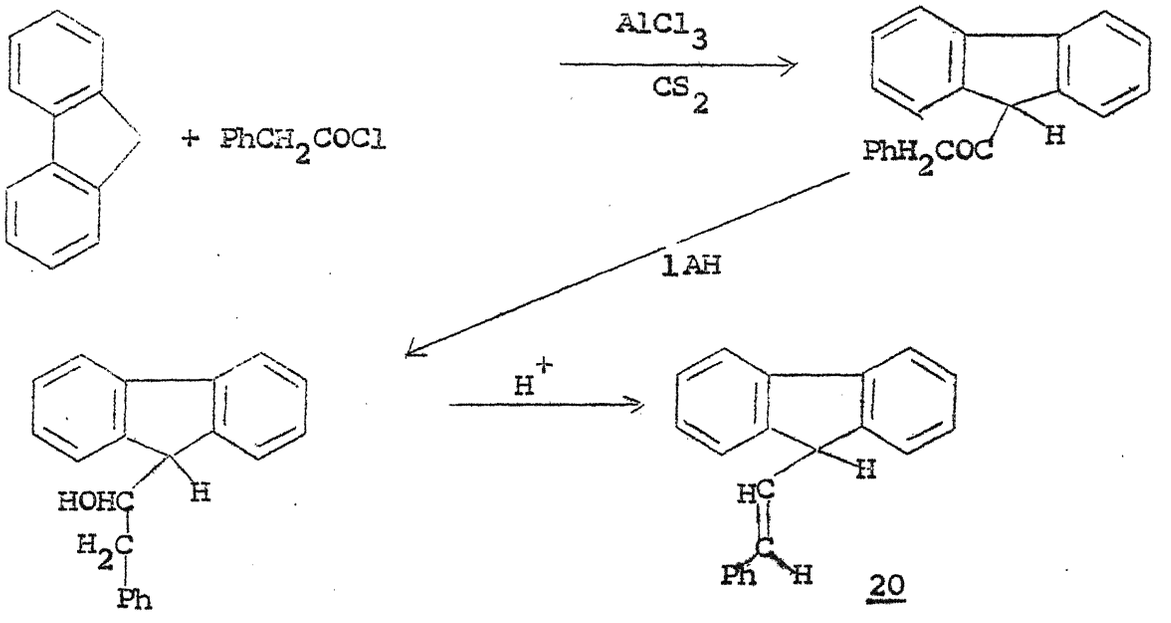
With the confirmation of structure 15 on basis of physical data and chemical degradation, efforts were made to discern the pathway by which the 11 → 15 change takes place. It was concluded that the key intermediate in this change is anion 18 arising from loss of elements of nitro group with concomitant ring rupture involving 19:



Anion 18 coud lead to 15 by three possible pathways:



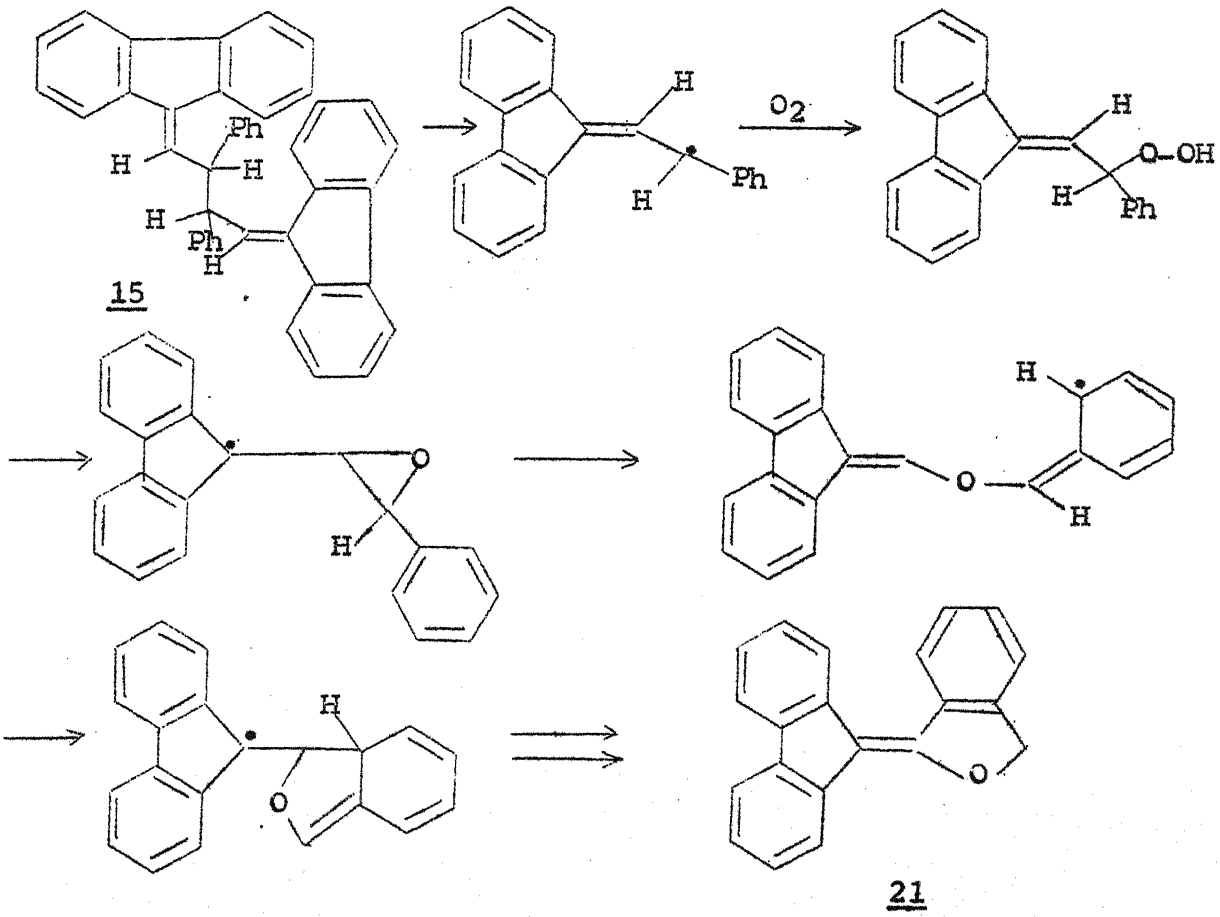
Consequently the conjugate acid of 18 was prepared[60,61] by the following sequence:



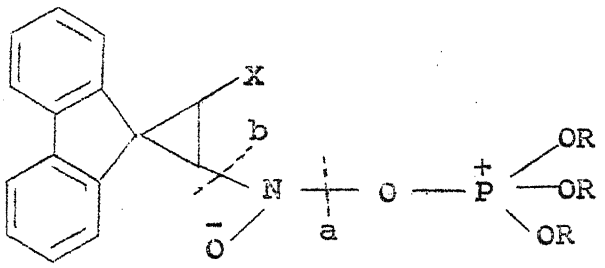
Reaction of 18 generated from 20 and NaH/DMF with either oxygen or with 11 gave no 15 thereby excluding pathways a and b and making c as the most reasonable one.

During one of the reactions involving 11 and triisopropyl phosphite after 75% reaction, accidental water failure caused the solvents to evaporate thus resulting in the rise in the inside temperature by nearly 30° and making the isolation of the system from air defective. Work-up involving chromatography over silica gel gave as the sole isolable product, a colourless crystalline compound mp 76-78° which was subsequently identified as phthalide on basis of analytical data, NMR, IR, MS and finally by comparison with authentic sample ! This unusual transformation probably involves fluorenylidine derivative 21 as the thermal

transformation product which undergoes ready hydrolysis in the column to give phthalide. It is reasonable to suppose that the fragmentation to monomeric unit observed during electron impact could take place also thermally. The further transformation of the resulting radical species, with oxygen can lead to 21:



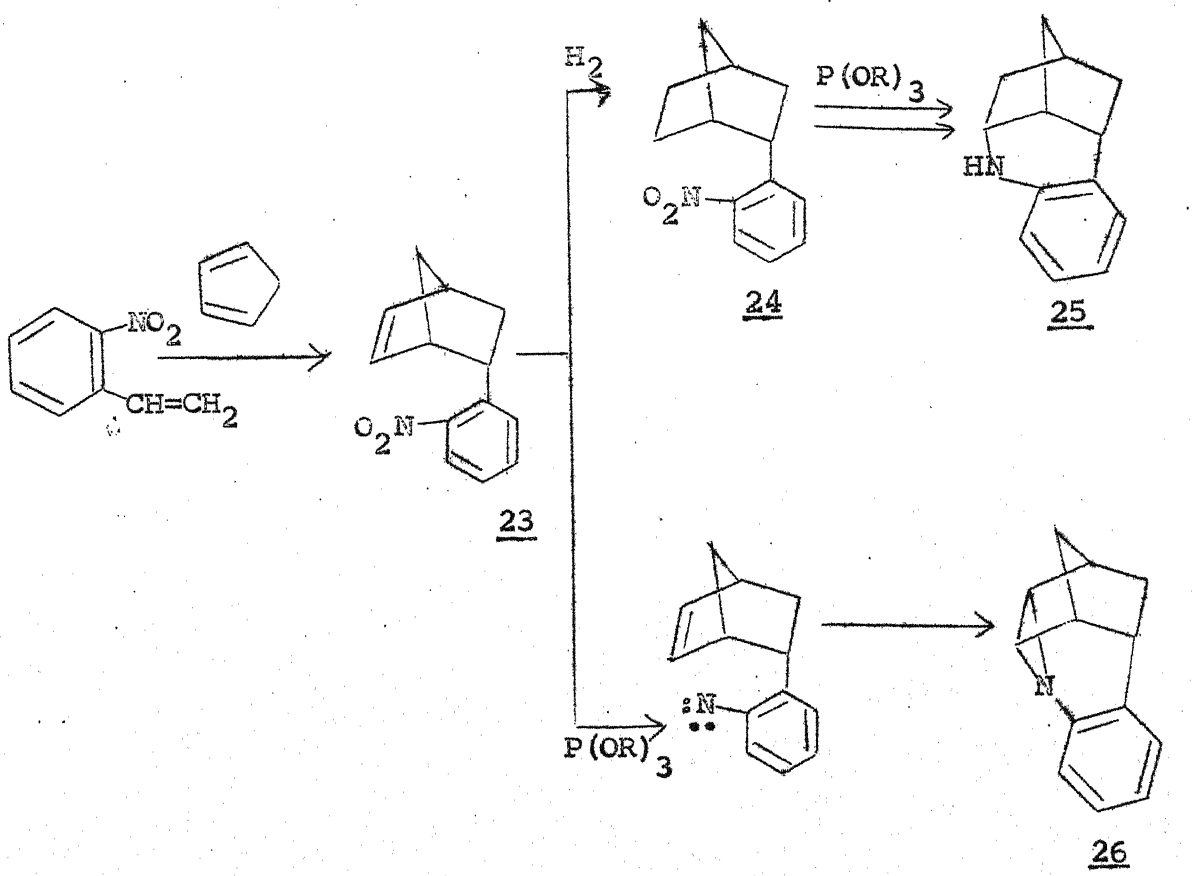
The differences in the behaviour of 10 and 11 can be analyzed in terms of N-O (path a) vs C-N (path b) bond repture of common intermediate 22:



22

The preference for path b with 11 must be due to possibility for enhanced stabilization of the resulting ion.

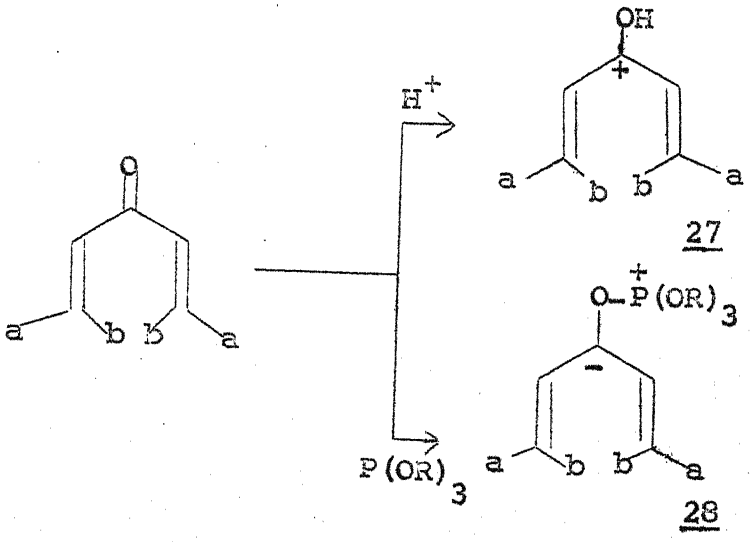
As part of ancillary programme, compound 23 was sought. It was hoped either 23 or its dihydro derivative 24 could undergo novel transannular reactions leading to 25 and 26 respectively with trialkyl phosphite:



24 25 23 26

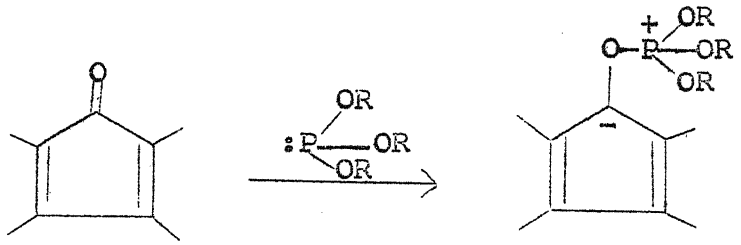
In the event however the attempted [4+2] addition of o-nitrostyrene with cyclopentadiene gave a complex mixture from which none of the expected 23 could be isolated. The work discussed thus far was concerned with novel behaviour of nucleophilic centres on nitrogen that are created with $P(OR)_3$. The following deals with creation of nucleophilic centres on carbon by reaction of selected carbonyl substrates with trialkyl phosphites and the possible exploitation of these species.

Cross conjugated dienones readily yield the 4-electron pentadienyl cation 27 by acceptance of electrophiles on oxygen. The converse situation leading to pentadienyl anion 28 can arise by acceptance of the nucleophile, $P(OR)_3$, by the carbonyl oxygen:

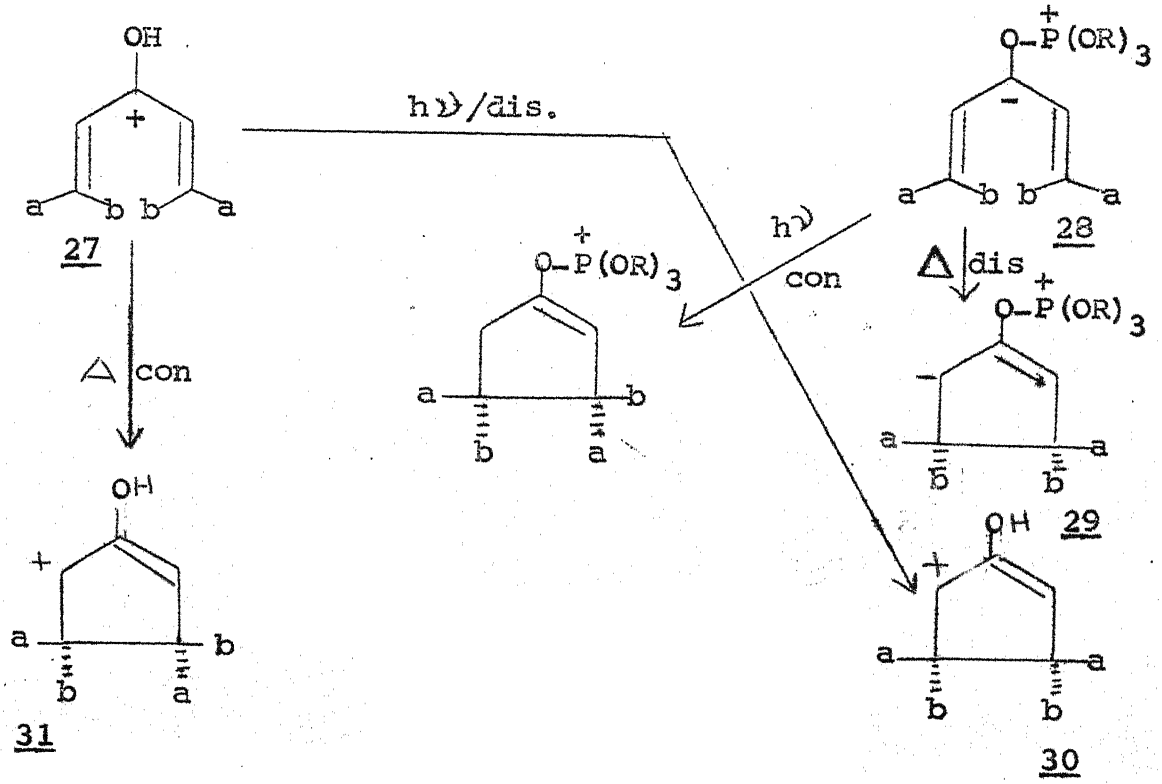


In fact, work from this laboratory as well as from others have clearly shown that the cyclopentadienide anion system can easily be produced by reaction of various P(III) compounds with

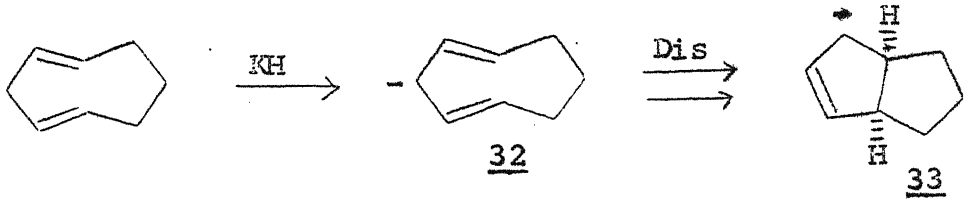
cyclopentadienone derivatives:[28-32]



The anion 28 can be expected to undergo stereospecific thermal dis-rotatory cyclization leading to the enol phosphate 29 which on hydrolysis would yield ketone 30. Parenthetically, the counterpart of 28, namely 27, readily undergoes thermal con-rotatory cyclization to give cation 31 as well as photochemical dis-rotatory cyclization to give 30.[62] Trialkylphosphite induced cyclization of cross conjugated dienone was consequently expected to provide a complementary method to acid induced cyclizations:

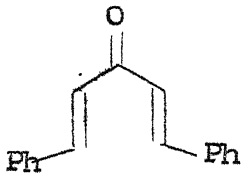


The known[63] stereospecific cyclization of anion intermediate 32 to 33 further supports the envisaged electrocyclic transformations of crosssed conjugated dienones with trialkylphosphites:

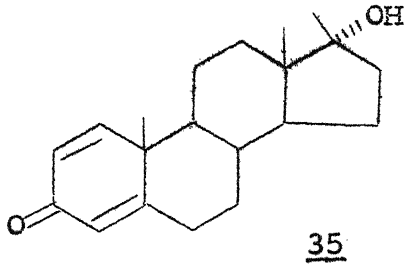


32 33

The acyclic 34 and the cyclic 35 were chosen for reaction with $P(OR)_3$:

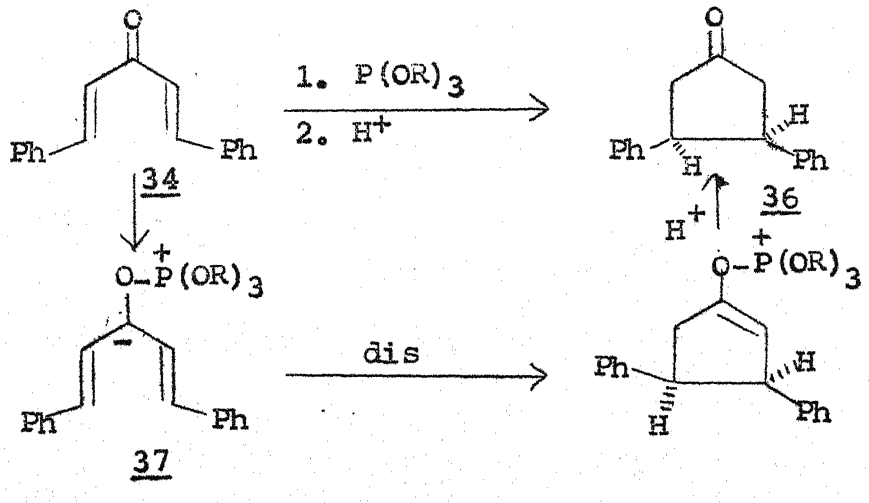


34

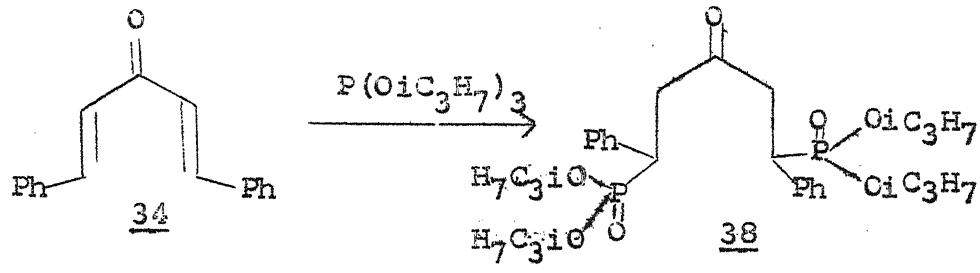


35

Dibenzal acetone 34 - readily available from acetone and benzaldehyde - was expected to give eventually the cis-diphenylcyclopentanone 36:



In the event reaction of 34 with neat refluxing triisopropyl-phosphite gave as the sole isolable product a colourless crystalline compound to which structure 38 is given:



The yield of 38 is 32% and the structural assignment is supported by IR, NMR and analysis.*

---

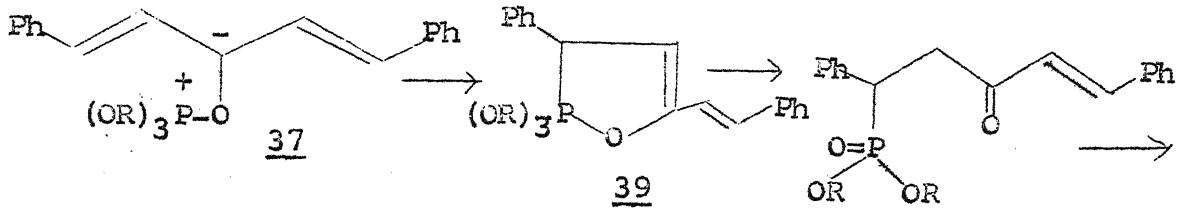
* 38, mp 128-29°.

IR : ν_{max} (KBr) (cm^{-1}): 1724 (-C=O), 1250 (P=O) and 992 (P-O-iPr).

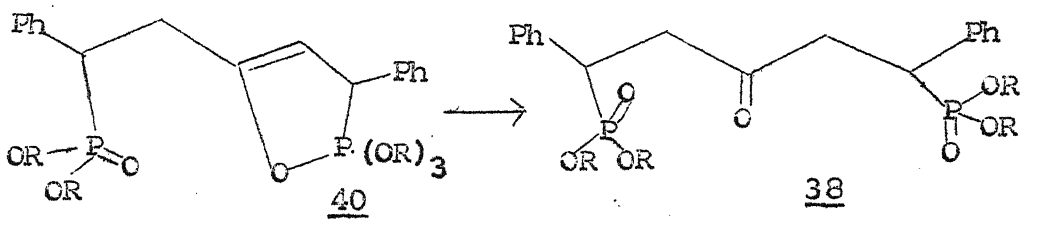
NMR: $\delta_{(CDCl_3)}$: 0.8 (d, J = 6 Hz, 6 protons, 1 isopropyl methyl), 1.19, 1.2 (d, J = 6 Hz, 18 protons, 3 isopropyl methyls).

TLC: Single spot R_f: 0.79 (Methanol).

The formation of 38 must be considered unusual because trialkyl phosphites normally do not form C-P bond. Consequently it is felt that 38 arises from the expected anion 37 by migration of the phosphorous moiety from oxygen to carbon:



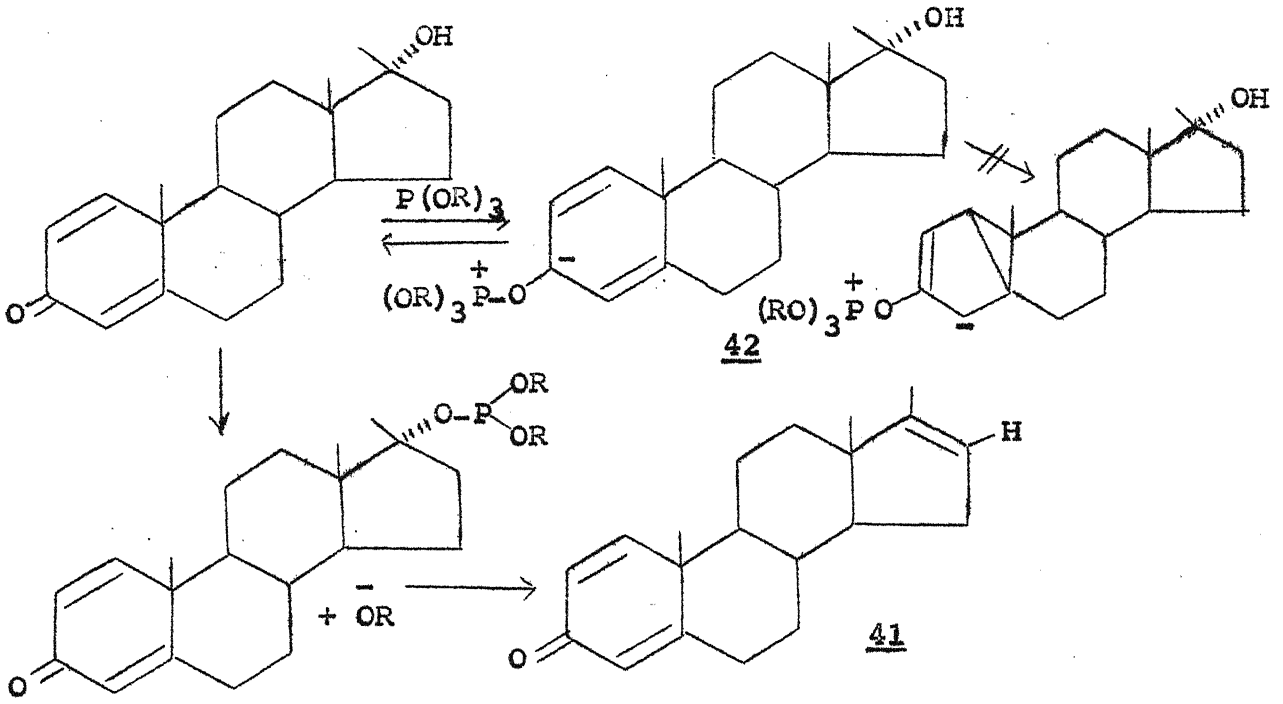
37 39



40 38

The formation of pentavalent phosphorous compounds related to 39 and 40 from α,β-unsaturated carbonyl compound and $P(OR)_3$ have already been reported.[64] Indeed results from the cyclic dienone 35 and triethylphosphite, where the envisaged oxygen to carbon migration is sterically impossible, supports these conclusions. Reaction of 35 with sodium dried triethylphosphite under conditions of 34 → 38 change merely gave olefin 41 by process apparently not affecting the dienone system. It is more probable that the expected anion 42 was produced in an equilibrium reaction, but since the oxygen to carbon migration of the phosphorous moiety is sterically not possible the cross - conjugated dienone system was not consumed. In any event it is clear that even in the stereochemically favoured 35, the cross - conjugated dienone system shows no tendency for cyclization in presence of trialkyl phosphites. The structure of 41 was established by analytical and spectral

data* and its formation can be readily accounted:



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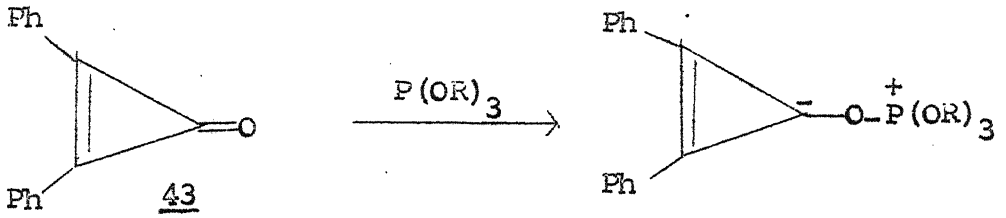
* 41, mp 130-31°.

IR : ν_{max} (KBr) (cm^{-1}) : 1658 (-C=O).

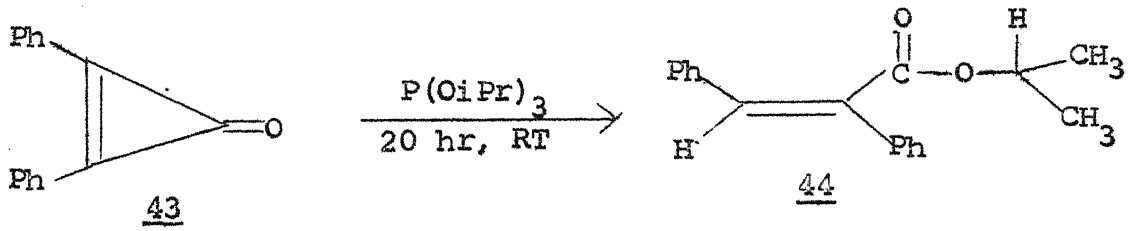
NMR: $\delta_{(CDCl_3)}$: 7.2 (d, J = 7 Hz, β-dienone proton), 6.25 (m, α-dienone protons) and 4.7 (broad, olefinic proton).

TLC: Single spot R_f : 0.56 (Benzene:Ethyl acetate 50:50).

The normal carbonyl $P(OR)_3$ interaction leading to carbon bases is not expected where anti-aromatic systems are involved as exemplified with diphenyl cyclopropenone (43):



Compound 43 was prepared from dibenzyl ketone by sequence involving halogenation and dehydrohalogenation.[65] Reaction of 43 with triisopropylphosphite, fresly distilled over sodium and under nitrogen, was complete in 20 hour (TLC). Work-up involving removal of solvent and chromatography gave as the sole isolable product isopropyl α-phenyl cinnamate 44:



Parenthetically TLC indicated that compound 44 was present even in the crude reaction mixture before work-up. The yield of 44 is 35% and its structure was established by analytical and spectral data.*

---

* 44, mp 72-73°.

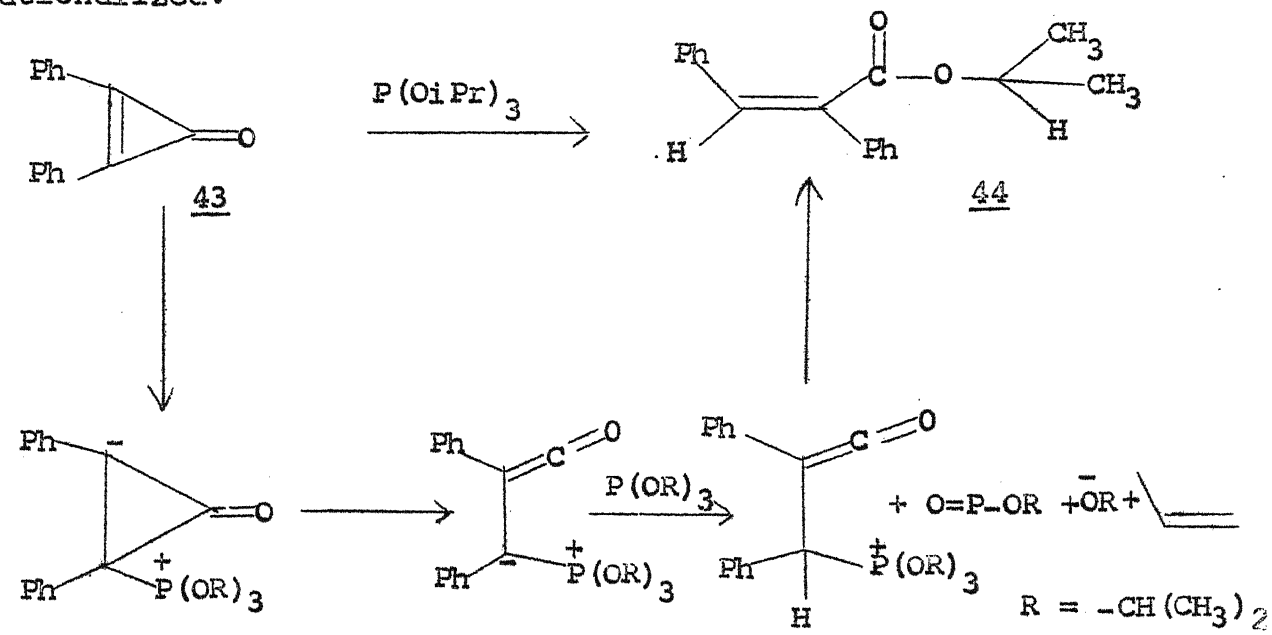
IR : ν_{max} (KBr) (cm^{-1}): 1695 (-C=O).

NMR: $\delta_{(CDCl_3)}$: 1.3 (d, J = 6 Hz, 6 protons, i-Pr), 5.3 (heptet, 1 proton), 7.3 (m, 10 aromatic protons) and 8.0 (s, olefinic proton).

MS : m/e - 266.

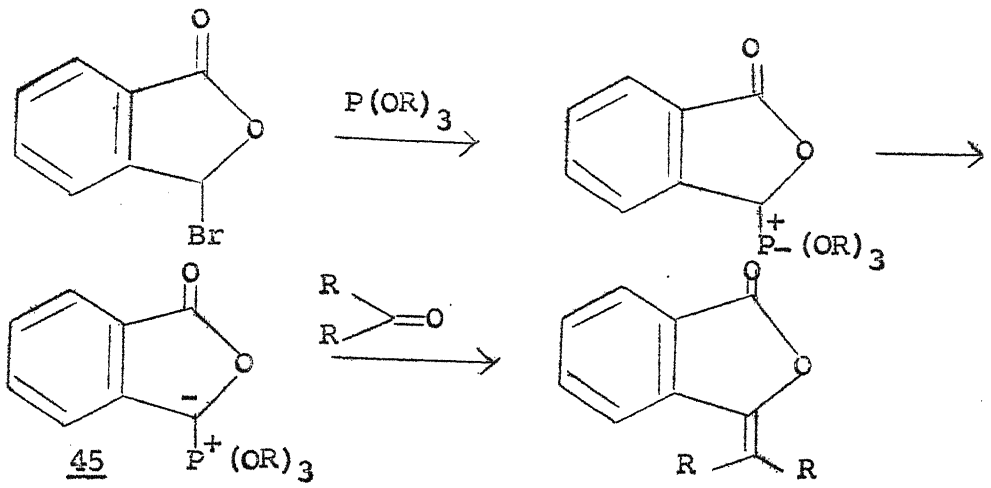
TLC: Single spot R_f: 0.68 (Benzene:Ethyl acetate, 50:50).

Blank experiments clearly ruled out the possibility of formation of 44 by trivial process involving the opening of 43 with isopropanol. The formation of 44 can be readily rationalized:



This sequence is in many ways similar to that envisaged for the 43 → 44 transformation with Ph_3P followed by ROH.[65a] Thus far, trialkylphosphite induced transformations were discussed on a mechanistic basis. In the course of this work few experiments were also carried out with a view of discovering reactions having preparative potential.

Synthon 45, which could transfer elements of phthalide unit to carbonyl substrate was sought from 3-bromophthalide:



When 3-bromophthalide and freshly distilled triisopropyl-phosphite in dry benzene was left stirred for 36 hr, a white crystalline compound precipitated which was subsequently identified as 46. The yield of 46 was 16% and structure is based on analytical and spectral data.* The formation of 46 is rationalized on basis of a combined Perkow-Arbusov pathway:

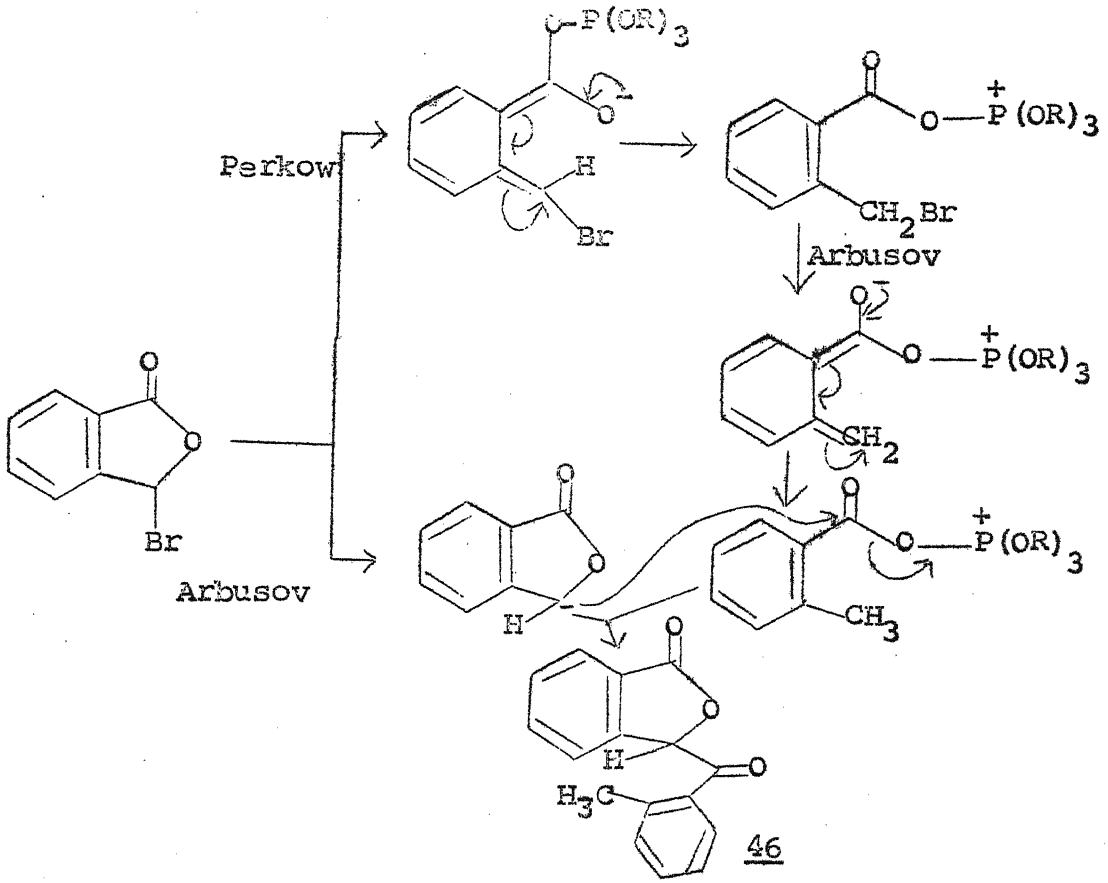
---

* 46, mp 157-58°.

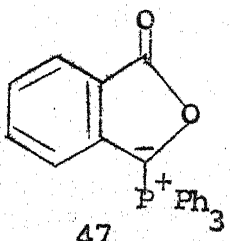
IR : ν_{max}(KBr) (cm^{-1}): 1767 (-C=O).

NMR: $\delta_{(CDCl_3)}$: 2.65 (s, aromatic methyl), 6.9 (s, t-proton) and 7.5 (m, aromatic protons).

TLC: Single spot R_f: 0.64 (Benzene:Ethyl acetate, 50:50).

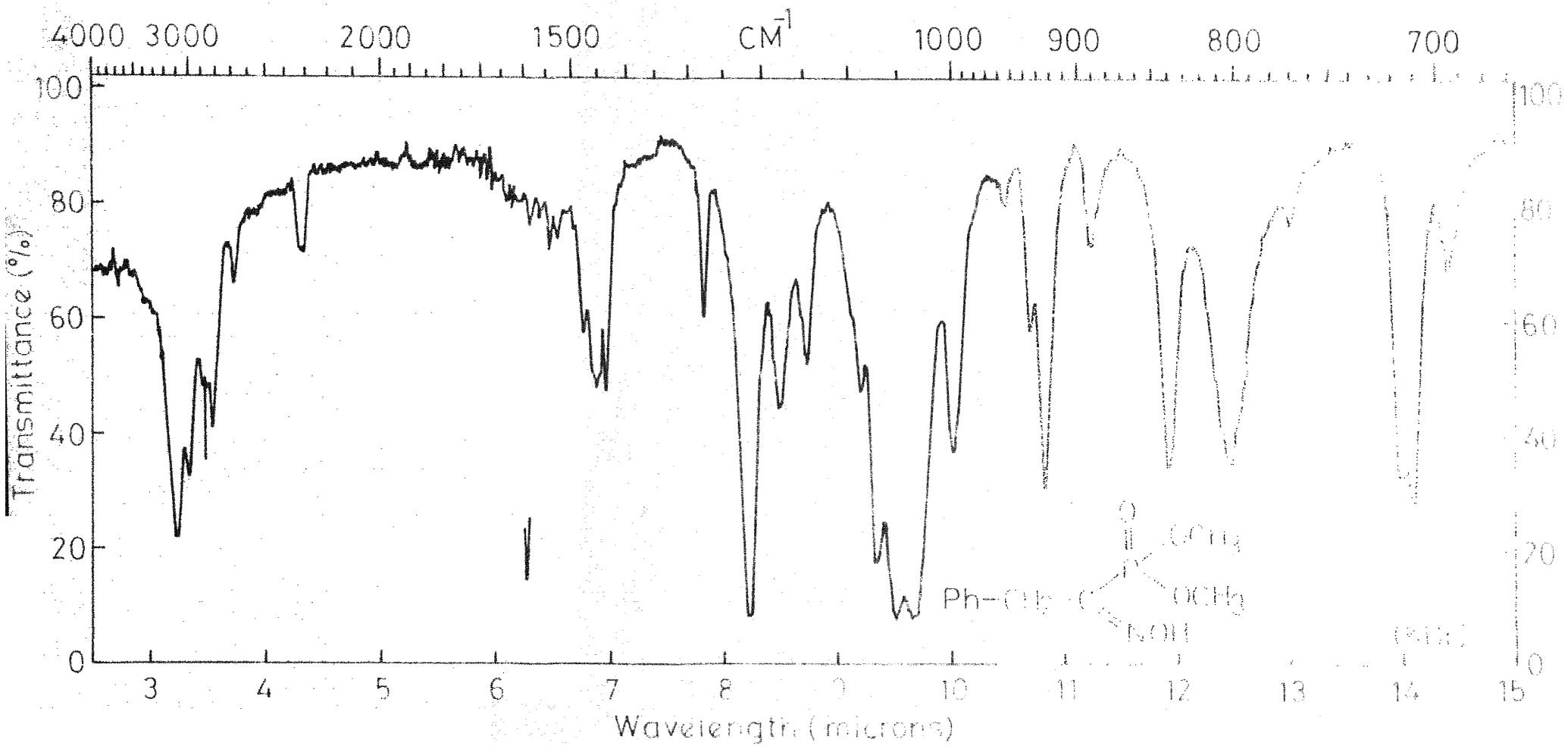


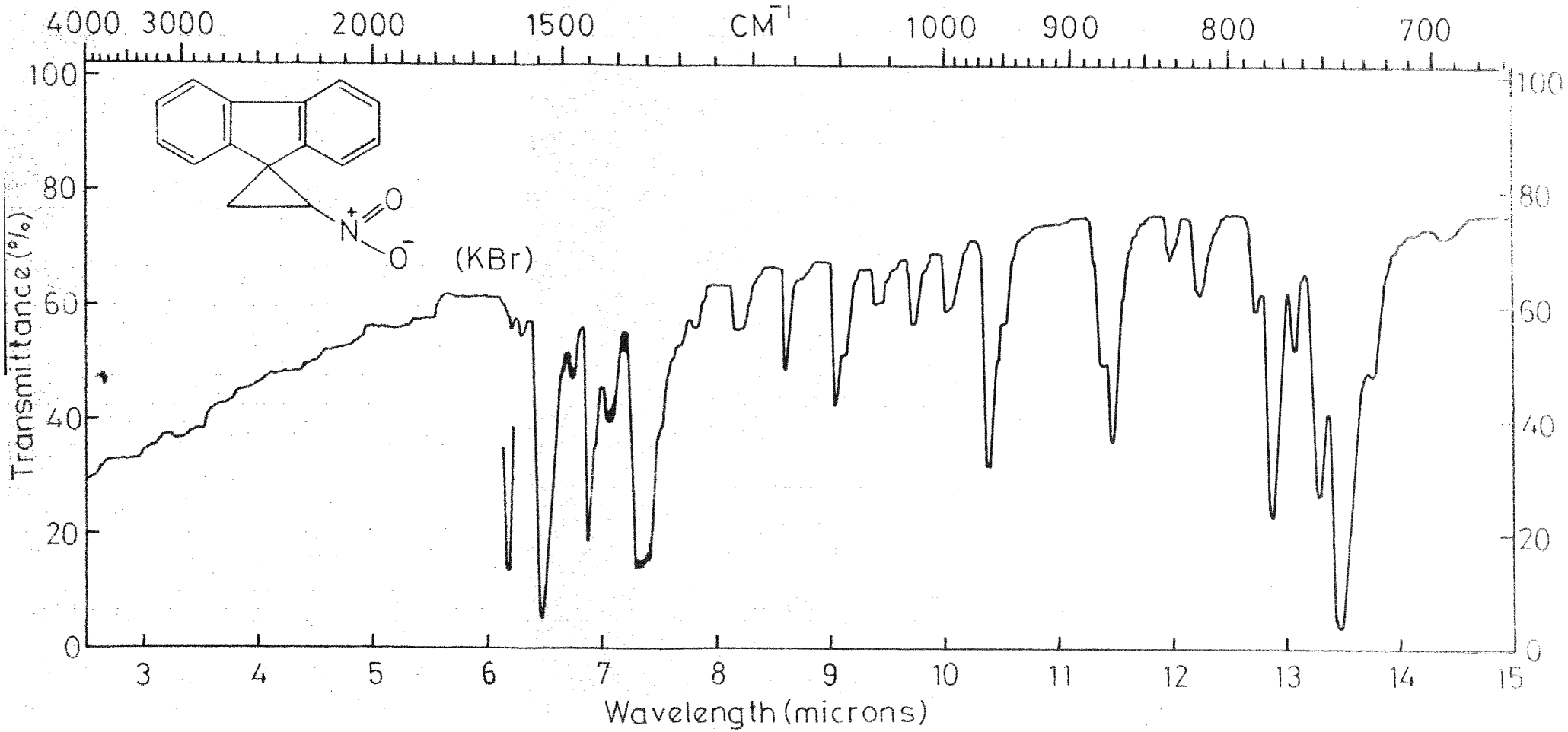
Examination of the benzene filtrate gave no additional products. Reaction of 3-bromophthalide in refluxing triisopropylphosphite gave small amounts of a crystalline yellow material, mp 281-282°, which has not been fully characterized. Subsequent to completion of this work, synthon 47 closely related to 45 has been prepared[66] and as expected 47 is a good phthalide transfer reagent.

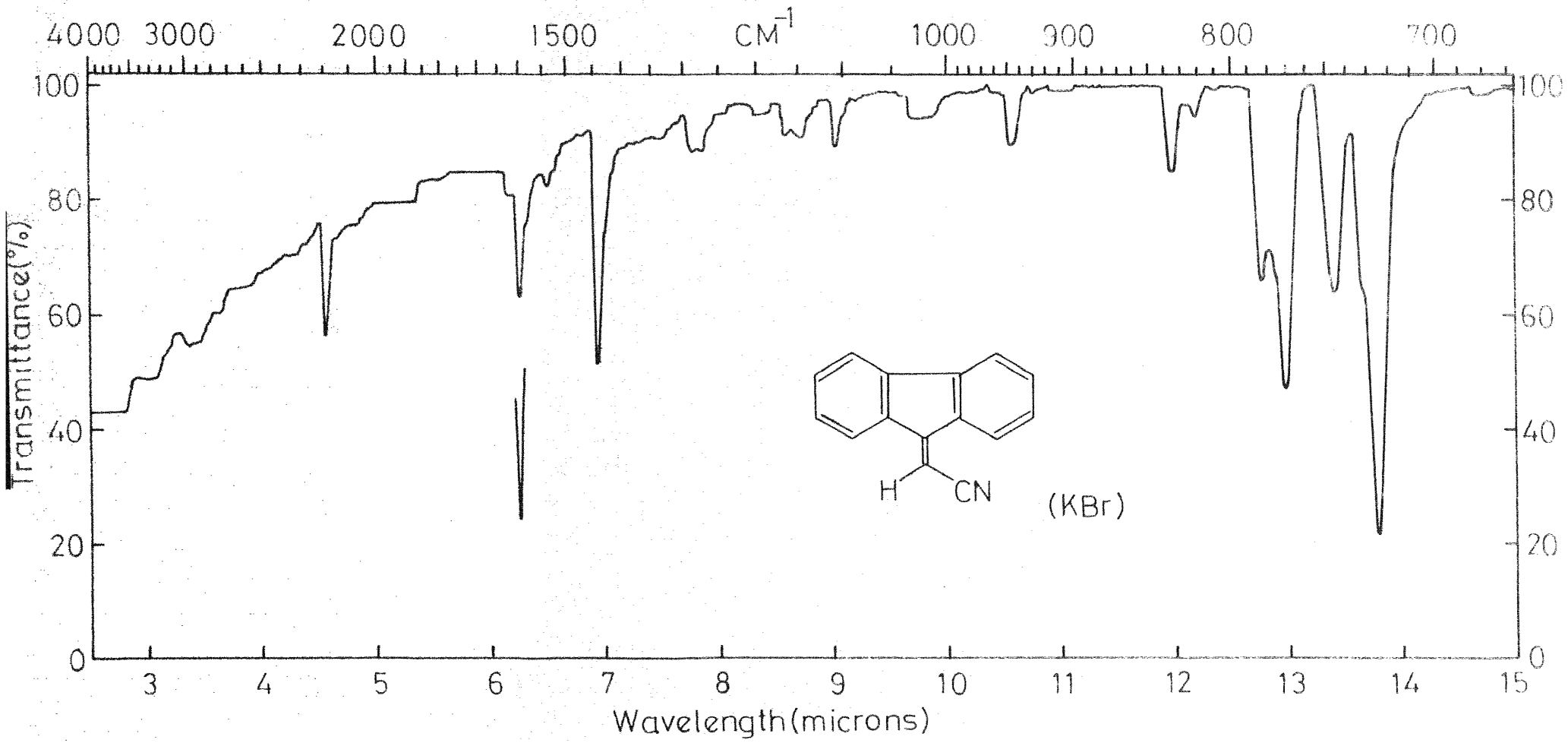


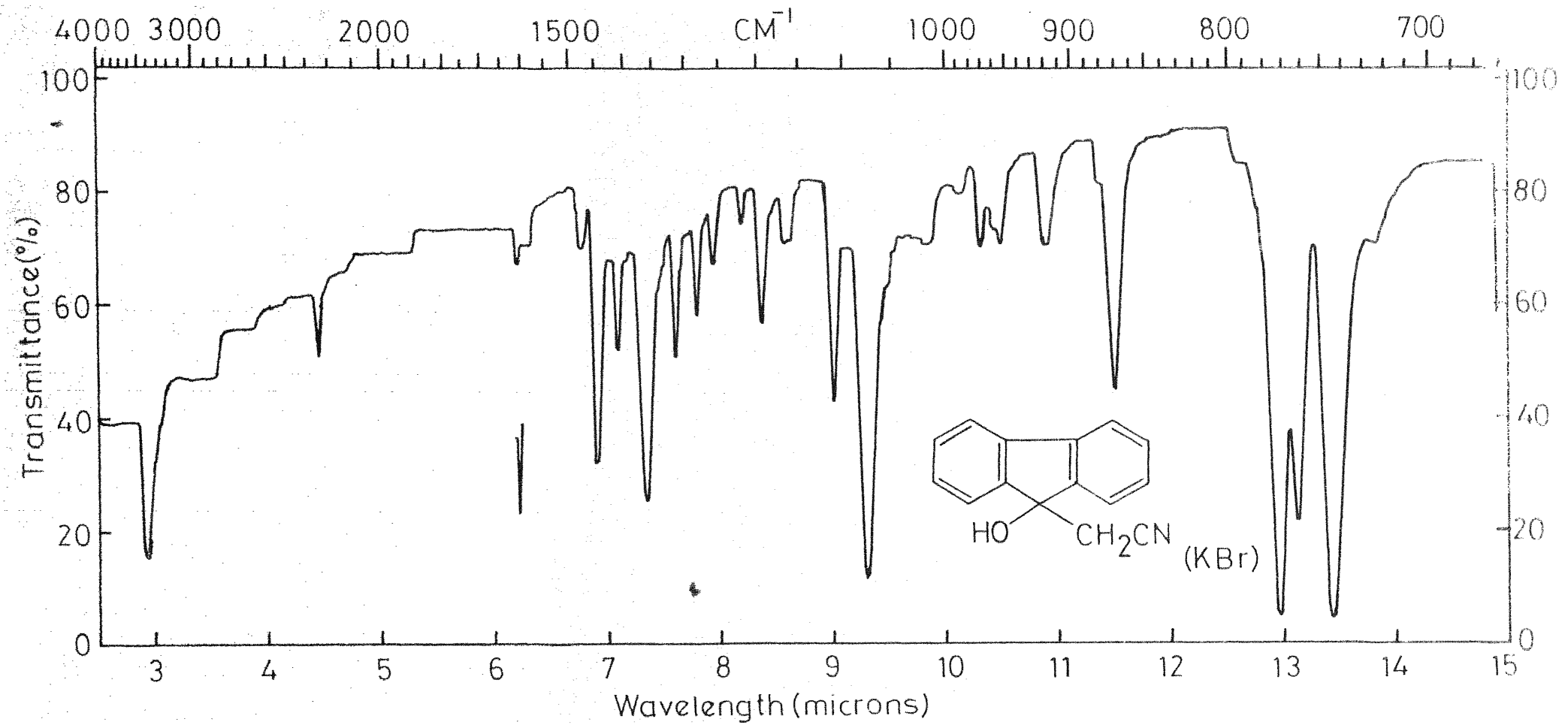
47

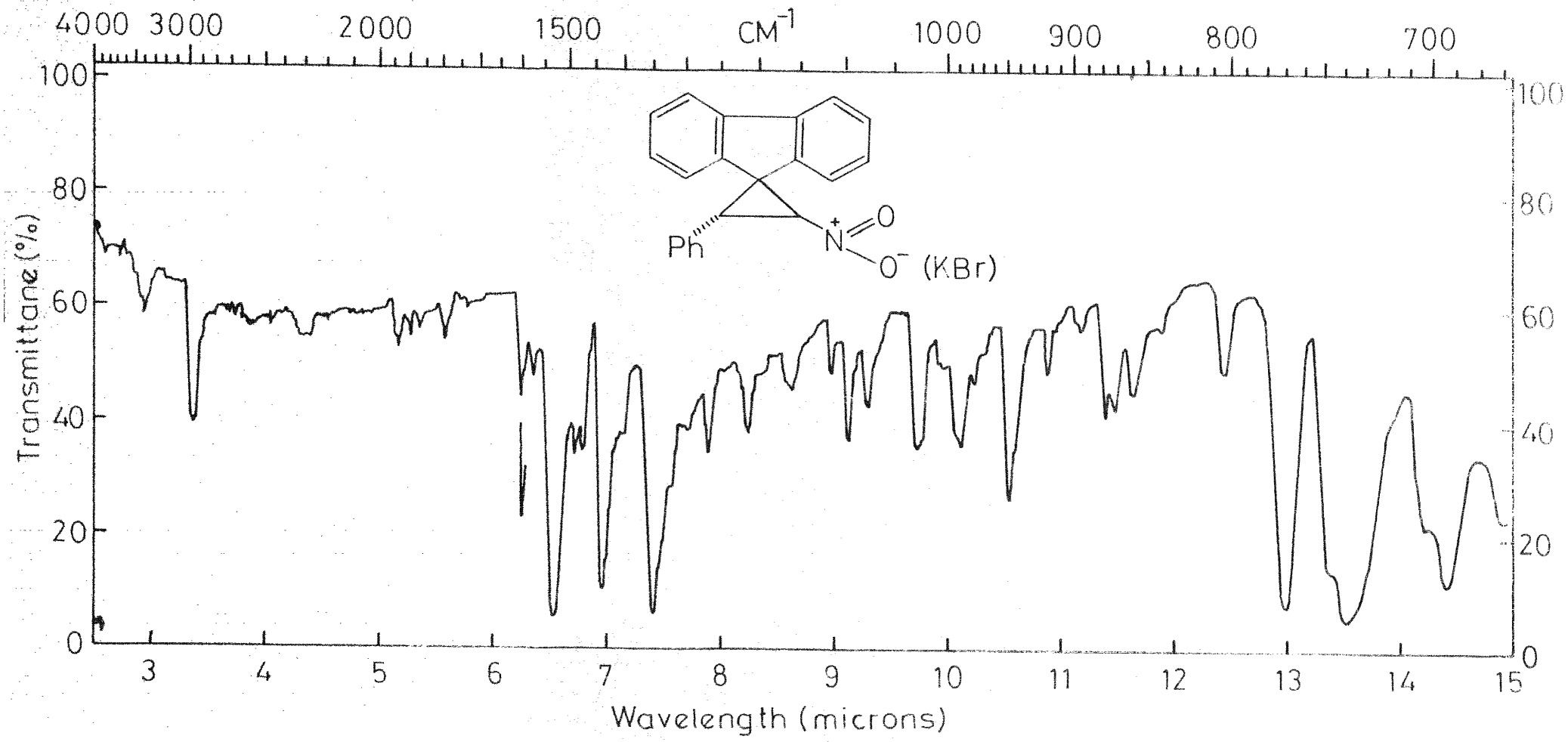
Finally the reaction of trialkyl phosphite with diverse cyclopropane carboxaldehydes and comphorquinone have been examined; however, the transformations were found to be complex and pure products could not be isolated.

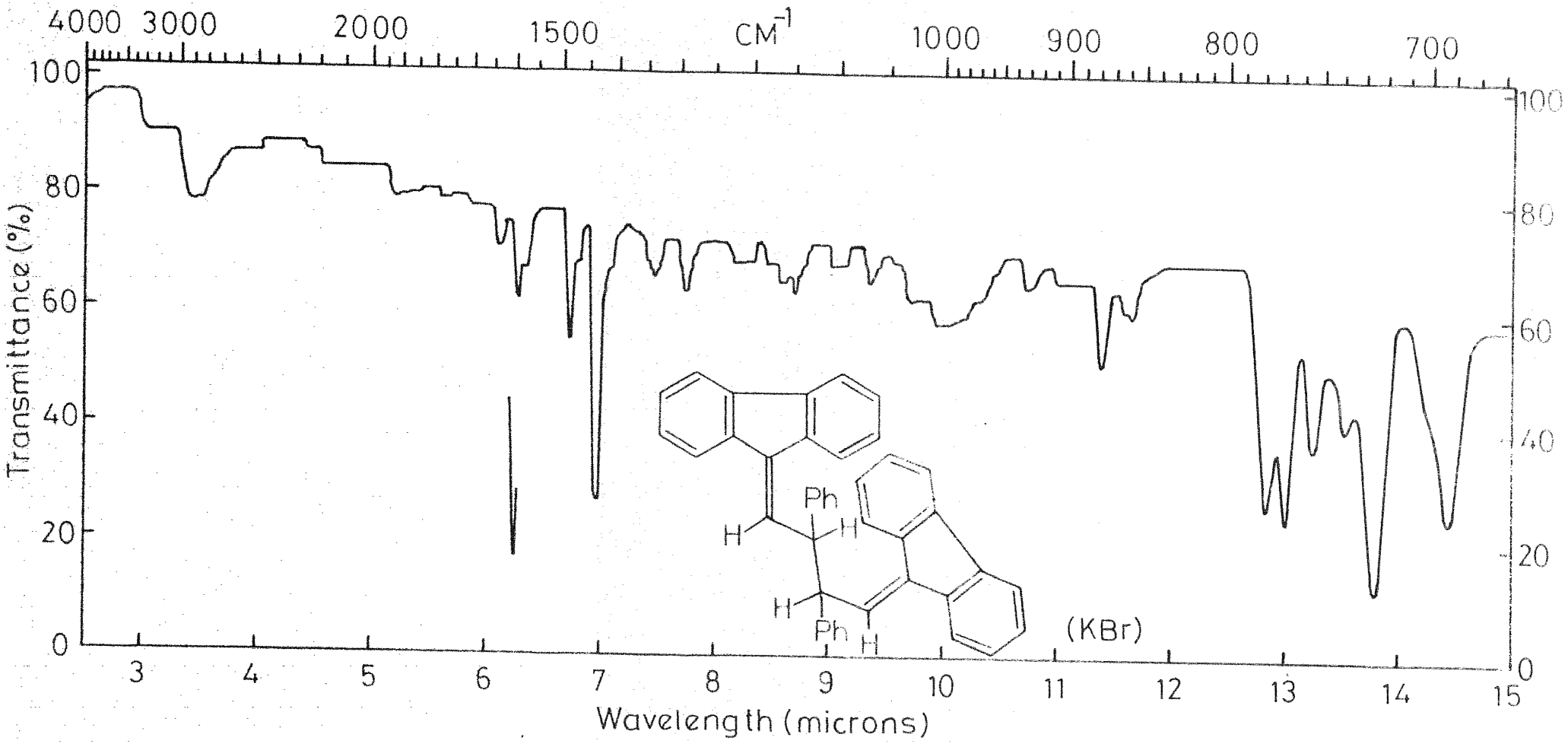

4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
100
80
60
40
20
0
Transmittance (%)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)
OCH3
OCH3
NOH

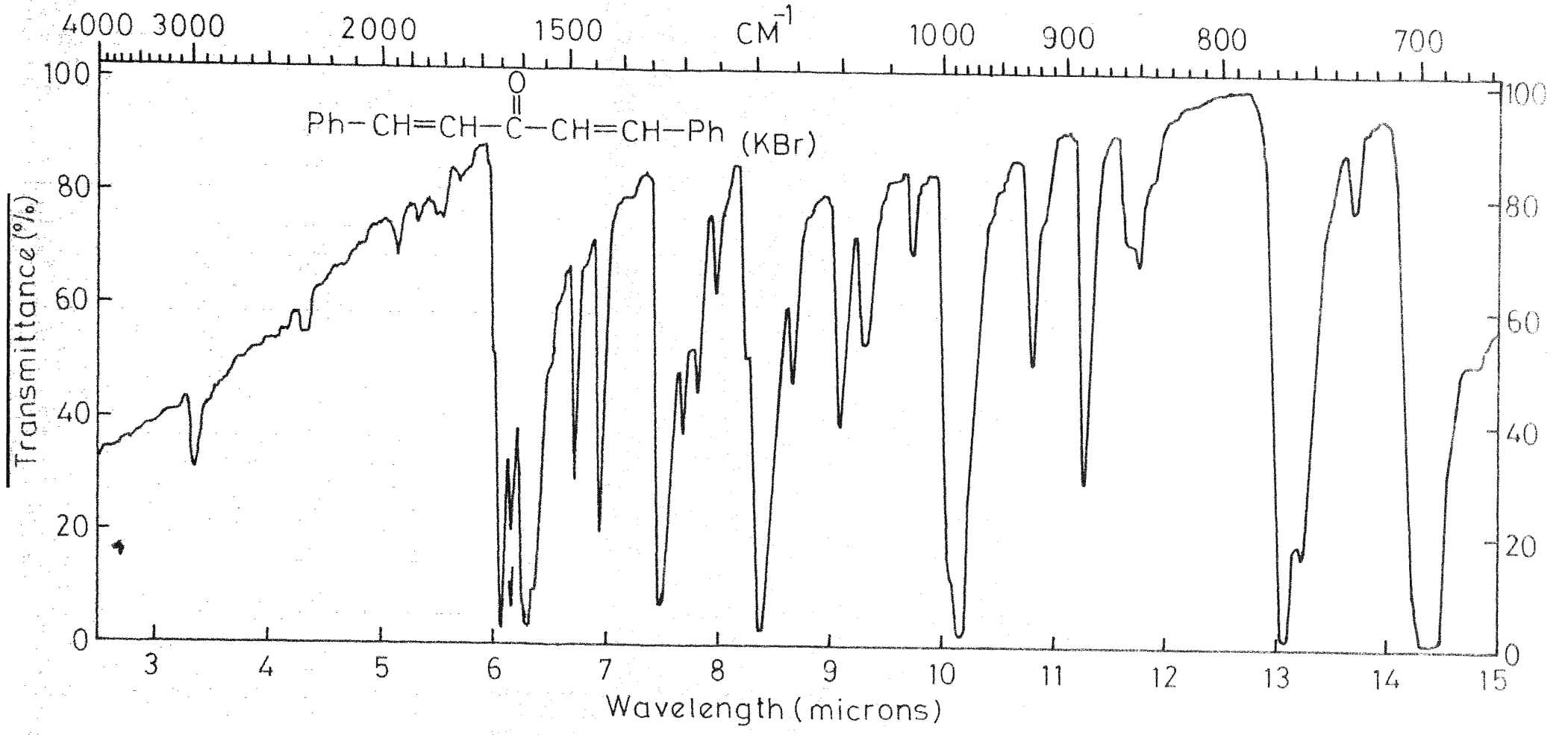

4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
100
80
60
40
20
0
Transmittance (%)
(KBr)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)

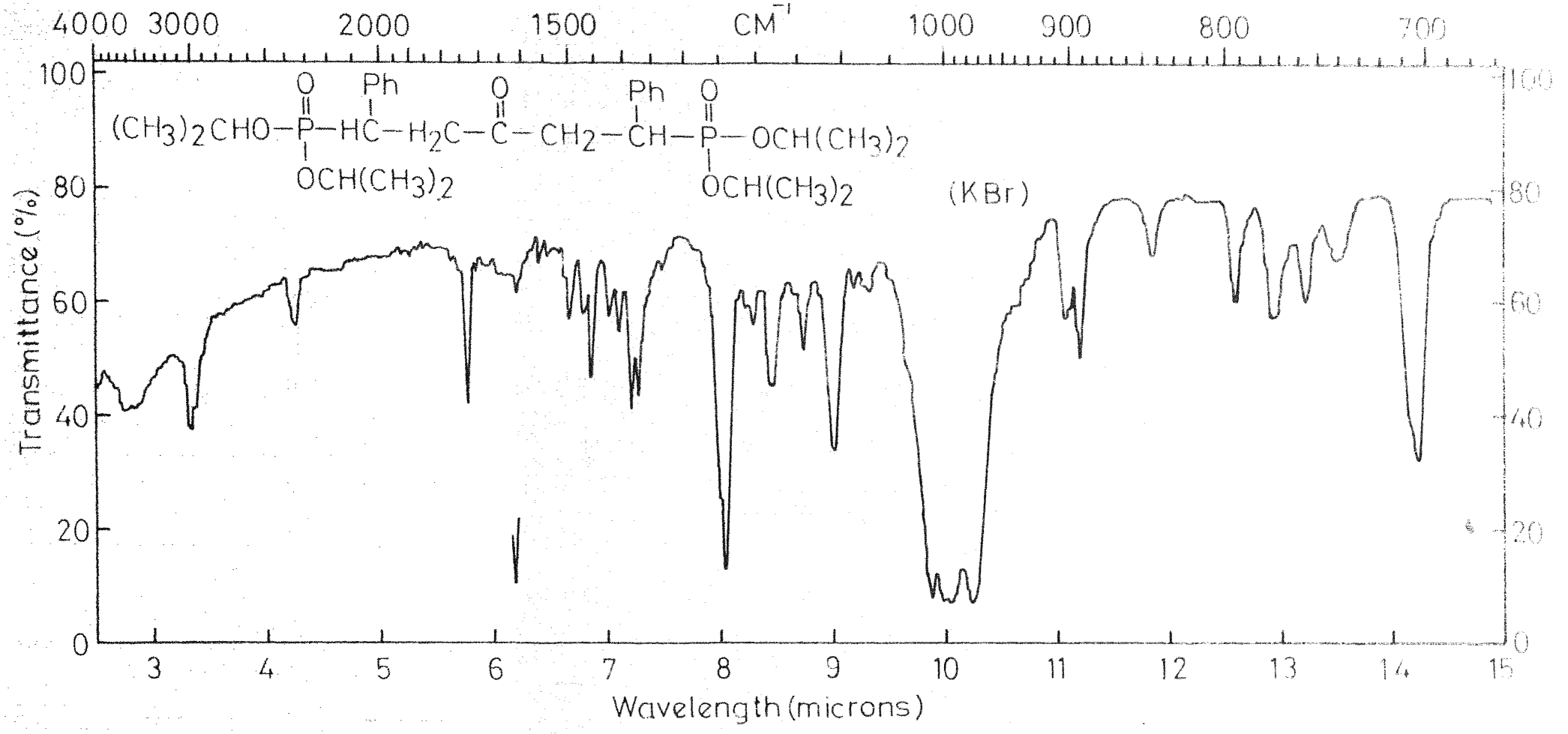

4000 3000 2000 1500 CM-1 1000 900 800 700
100
80
60
40
20
0
Transmittance(%)
H
CN
(KBr)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength(microns)

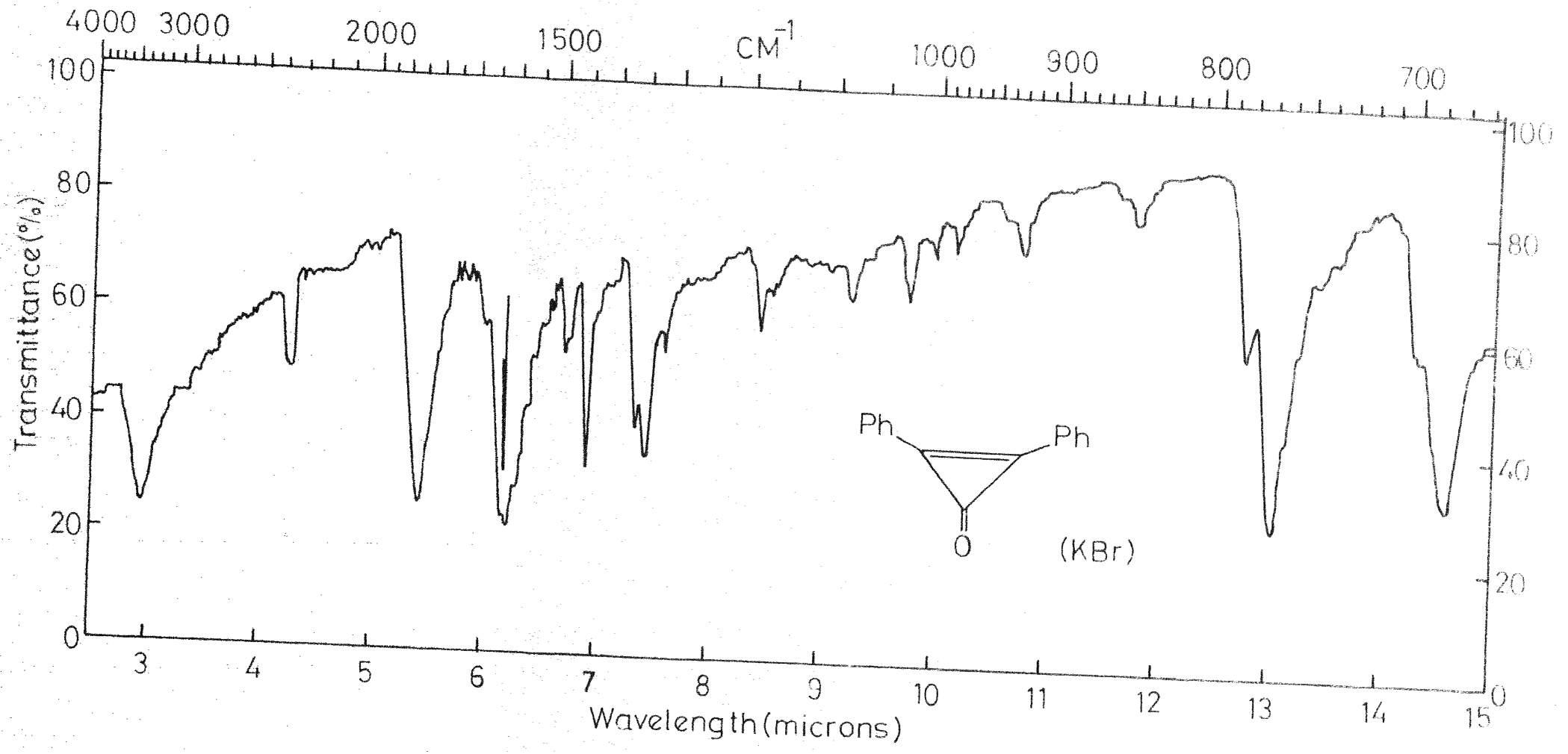

4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
100
80
60
40
20
0
Transmittance(%)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)
HO
CH2CN
(KBr)

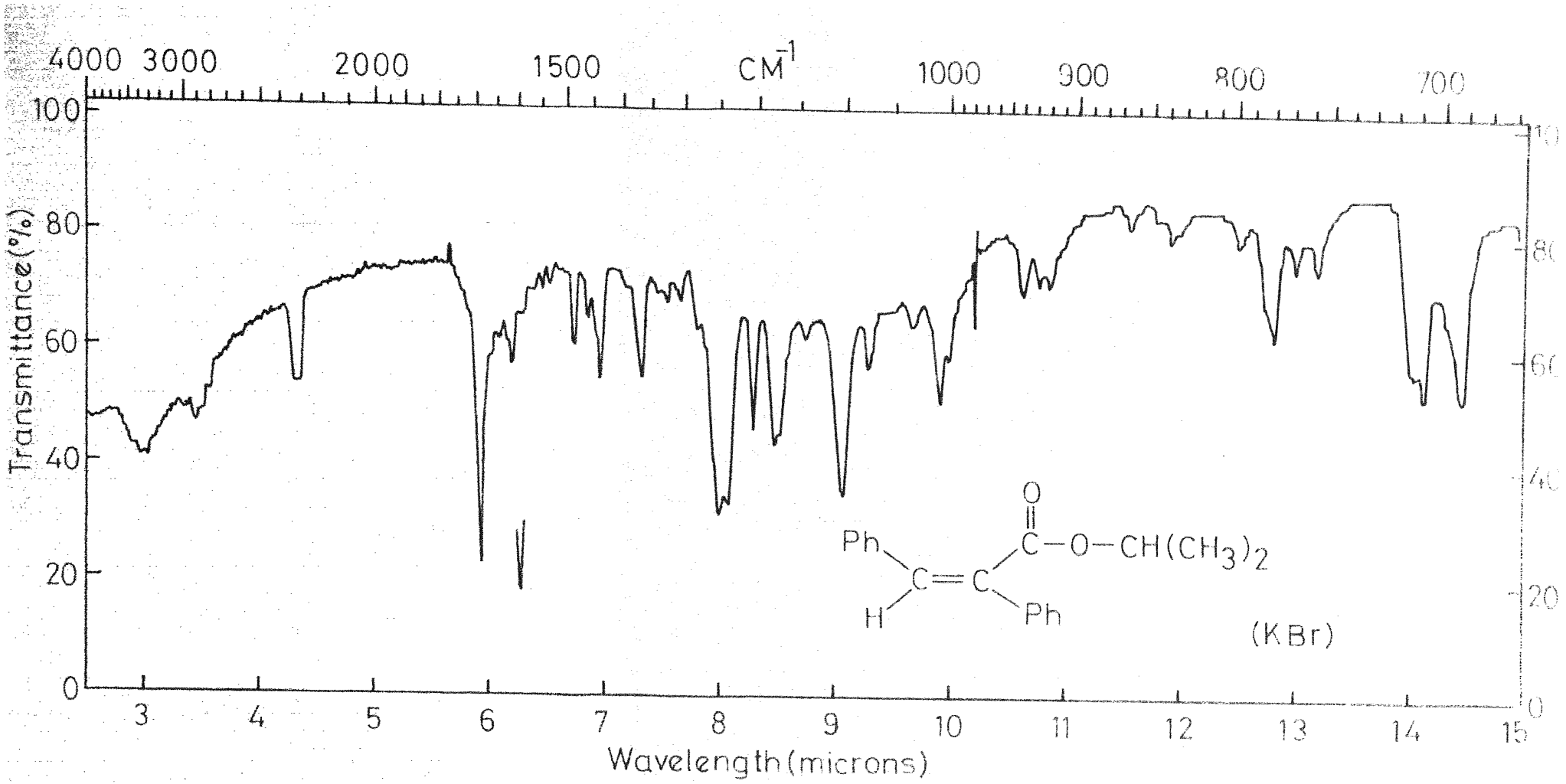

4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
100
80
60
40
20
0
Transmittance (%)
Ph
N
O
O⁻
(KBr)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)

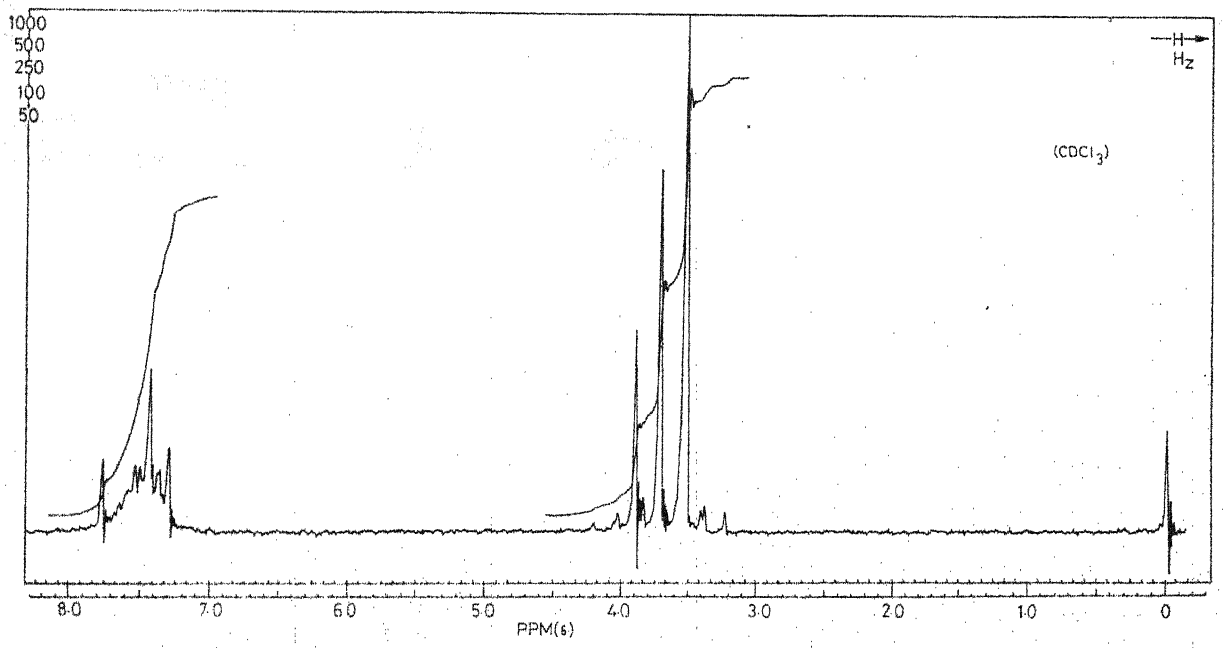

4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
100
80
60
40
20
0
Transmittance (%)
Ph
H
H
H
Ph
H
(KBr)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)


4000 3000
2000
1500
CM-1
1000
900
800
700
100
80
60
40
20
0
Ph-CH=CH-C-CH=CH-Ph
O
(KBr)
Transmittance (%)
3
4
5
6
7
8
9
10
11
12
13
14
15
Wavelength (microns)

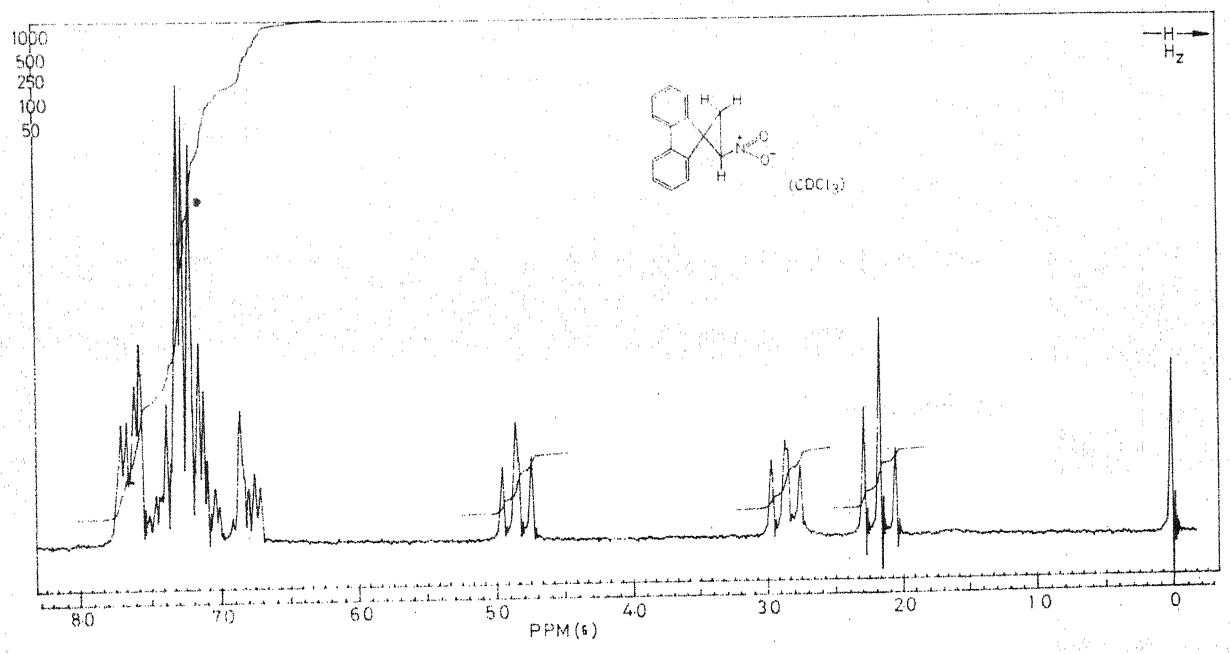

4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
100
80
60
40
20
0
Transmittance (%)
(CH3)2CHO–P(=O)(OCH(CH3)2)–HC(Ph)–H2C–C(=O)–CH2–CH(Ph)–P(=O)(OCH(CH3)2)–OCH(CH3)2
(KBr)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)

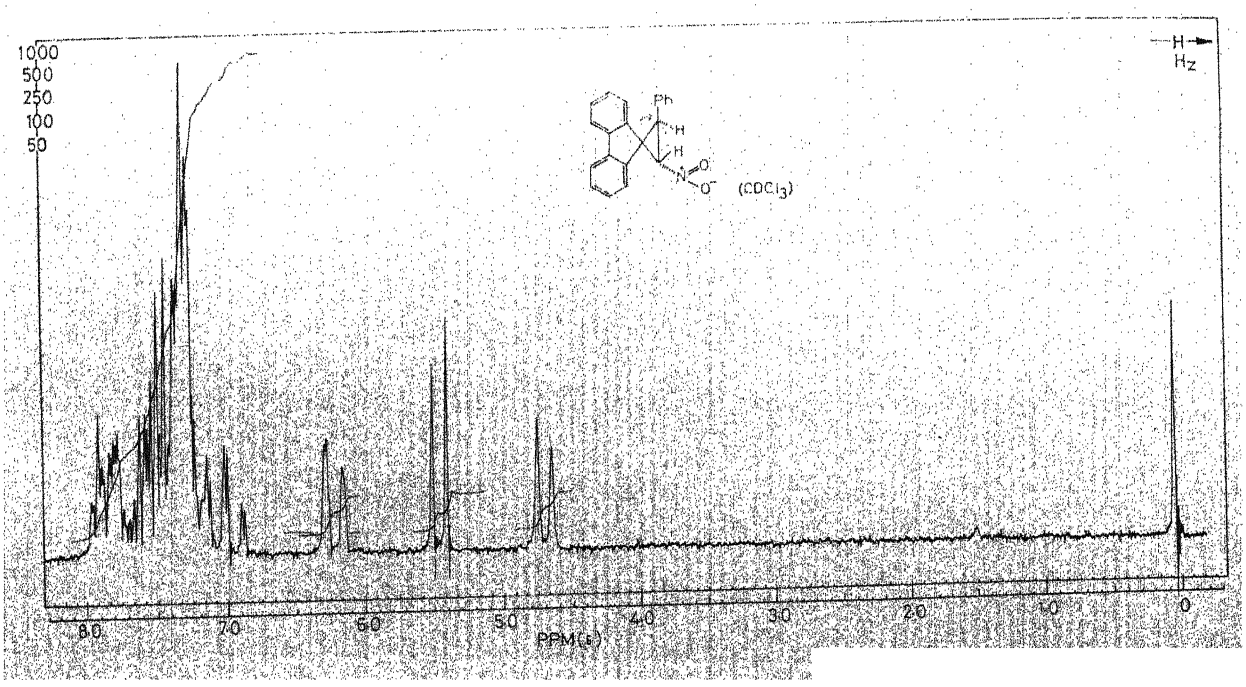

4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
100
80
60
40
20
0
Transmittance (%)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)
Ph
Ph
O
(KBr)

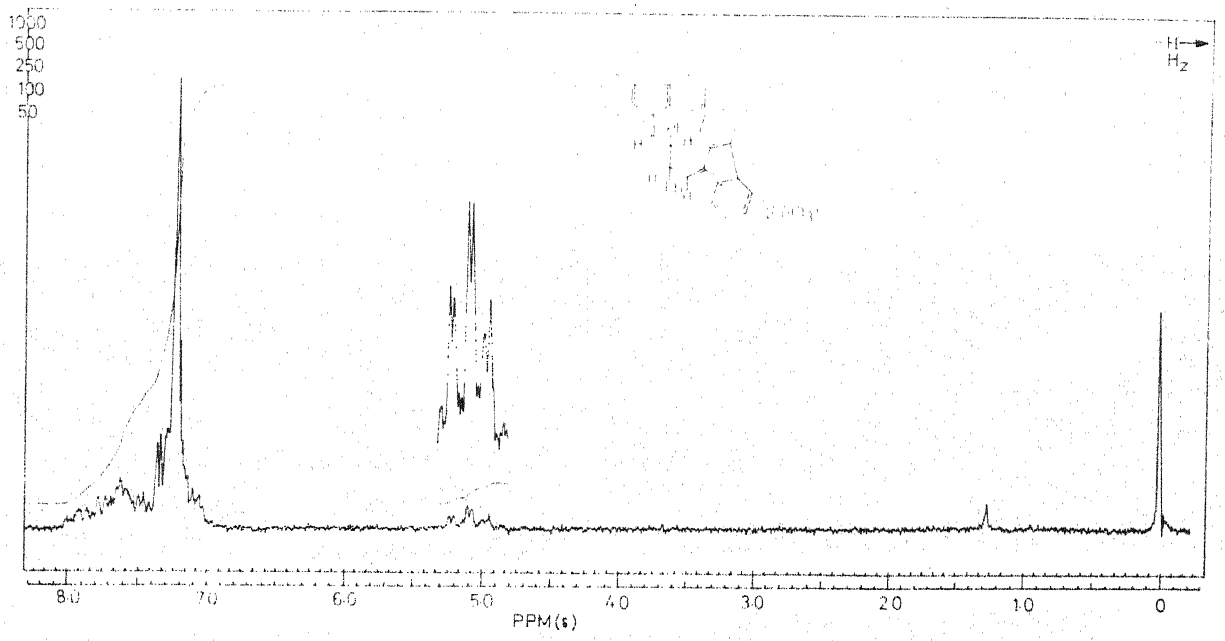

4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
Transmittance(%)
100
80
60
40
20
0
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength(microns)
Ph
C
C
H
O
C—O—CH(CH3)2
Ph
(KBr)

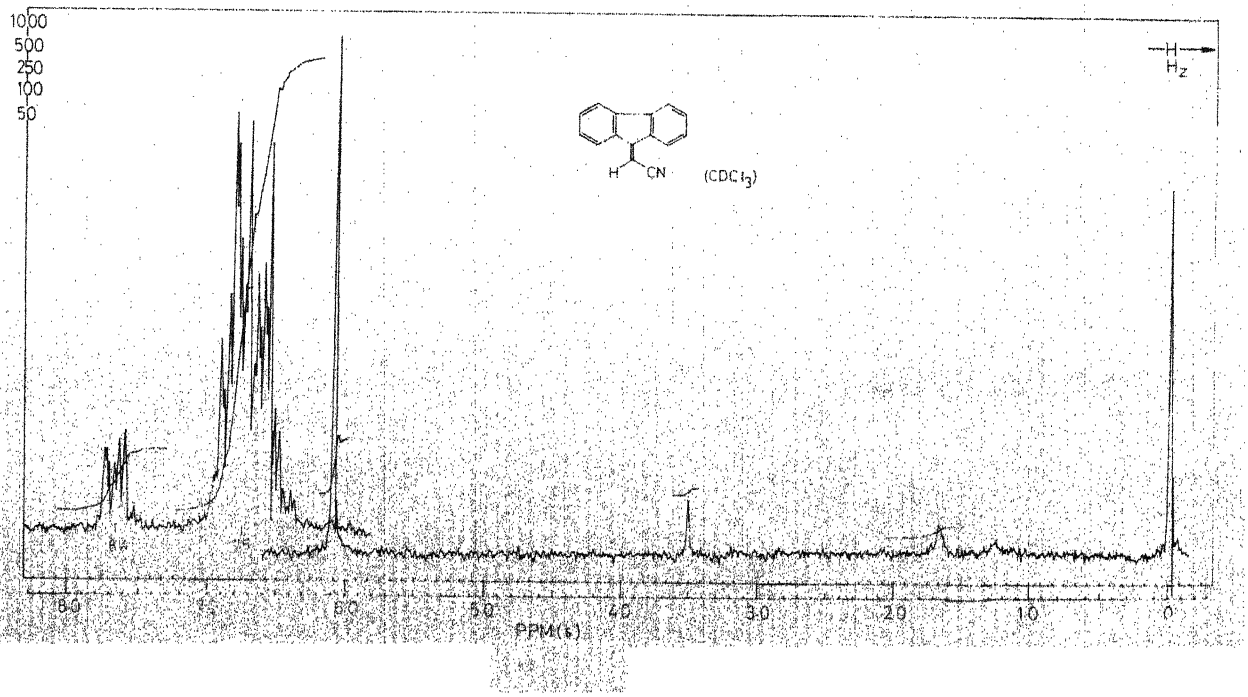


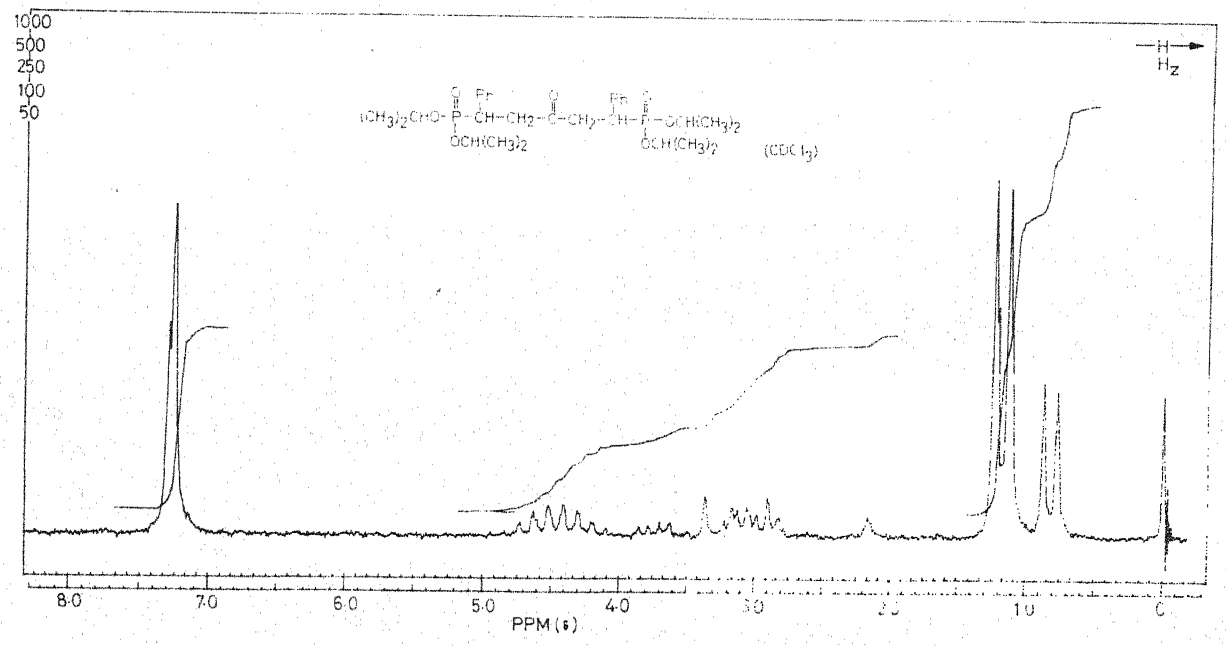
NMR Spectrum of Phenyl Acetyl Dimethylphosphonate Oxime (4)

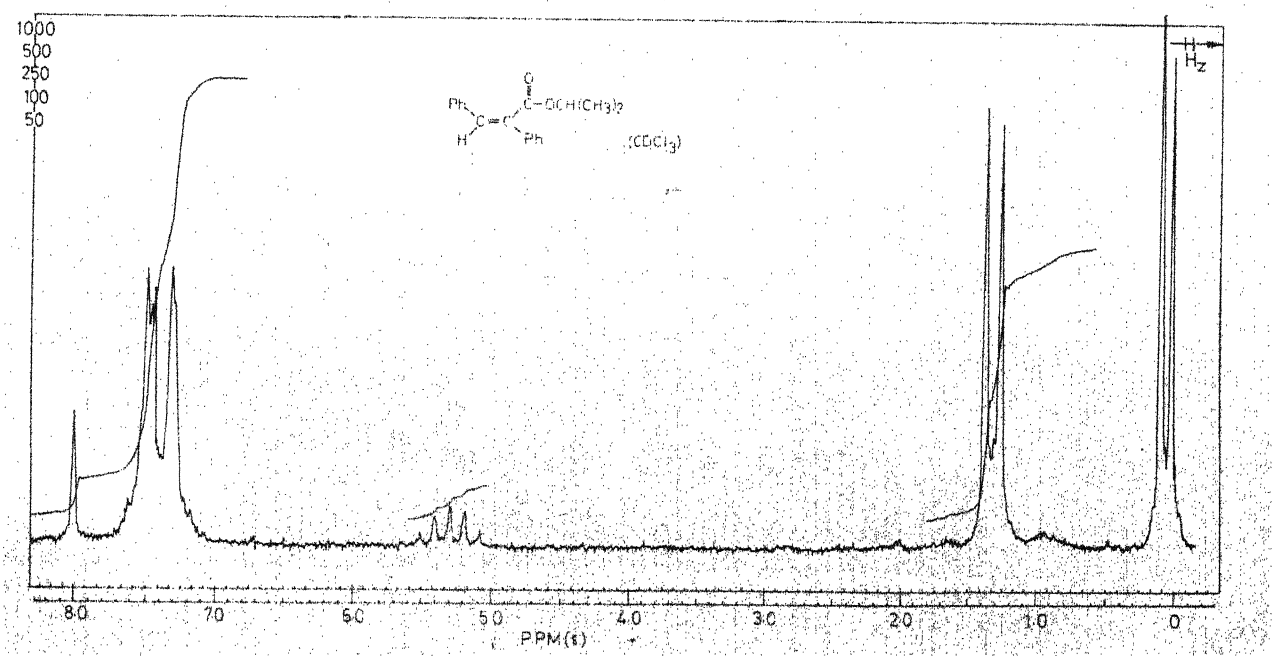

1000
500
250
100
50
H
Hz
(CDCl3)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM(δ)


1000
500
250
100
50
H
Hz
Ph
(CDCl3)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM(δ)


1000
500
250
100
50
H
Hz
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM(δ)


1000
500
250
100
50
H
Hz
H
CN
(CDCl3)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
PPM(δ)


1000
500
250
100
50
H
Hz
(CDCl3)
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0
PPM (δ)


1000
500
250
100
50
H
Hz
Ph
H
Ph
(CDCl3)
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0
PPM (δ)

II.E EXPERIMENTAL

GENERAL

Melting points were taken on a Fisher-John melting point apparatus and are uncorrected. Infrared spectra were recorded either on a Perkin-Elmer-700 or Perkin Elmer-137 or Perkin Elmer-521 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were determined with $CDCl_3$ solution on a Varian A-60 spectrometer using TMS as internal standard.

Silica gel G (Stahl) with calcium sulfate binder was used for thin layer chromatography (TLC). Column chromatography was performed either with silica gel (BDH) or with alumina, columns being made from its slurry in petroleum ether (bp 40-60°).

Preparation of Triisopropylphosphite

To a stirred and ice-cooled solution of absolute isopropanol (90 g, 116 ml, 1.5 mol) and freshly distilled N,N-dimethylaniline (181.5 g, 183 ml, 1.5 mol) in dry petroleum ether (bp 40-60°, 500 ml) was added in drops, over 0.5 hour a solution of phosphorous trichloride (68.75 g, 44 ml, 0.5 mol) in dry petroleum ether (bp 40-60°, 200 ml). The reaction mixture was then refluxed gently for one hour without stirring and the suspension containing dimethylamine hydrochloride was cooled,

filtered, the cake of the amine salt well compressed and washed with dry petroleum ether (bp 40-60°, 5 x 50 ml). The filtrate and washings were combined, concentrated by distillation on a water bath and distilled, bp 64-65°/8-10 mm (lit.[67] bp 60-61°/10mm yield 66.2 g (63%).

β-Nitrostyrene

To an ice-salt cooled and stirred mixture of distilled nitromethane (61 g, 1 mol), freshly distilled benzaldehyde (106 g, 1 mol) and AR methanol (170 ml) was added in drops-maintaining the inside temperature at 10-15° — a solution of sodium hydroxide in water (35 g, 85 ml, 0.875 mol) over a period of 0.5 hour. After additional 0.25 hour, the pasty mass was converted to a clear solution by the addition of 500 ml of iced water and poured into dil. hydrochloric acid (made by diluting 170 ml of conc. hydrochloric acid with 250 ml of water) as a thin stream. A pale yellow crystalline mass separated immediately. The reaction mixture was filtered, washed with water until free from chloride, melted in a beaker immersed in hot water, the lower layer of nitro styrene frozen by cooling and the crude product crystallized from hot 95% alcohol; yield 94 g (75%), mp 57-58° (lit.[68] mp 57-58°).

IR: ν_{max} (KBr) (cm^{-1}): 1613, 1495 (NO_2 asym.), 1337 (NO_2 sym.).

Reaction of β-Nitrostyrene with Trimethylphosphite: Isolation of Phenyl acetyl dimethylphosphonate oxime (4)

Under nitrogen to a stirred, freshly distilled trimethyl phosphite (2.3 ml) was added β-nitrostyrene (1.49 g, 0.01 mol). Within 5 minutes the reaction became exothermic and the inside temperature rose to 185°. The resulting red mixture was further stirred for 10 hr, solvents distilled off (135-145°/8-10 mm) and the residue chromatographed on silica gel. Elution with ethyl-acetate/methanol (50:50) gave a solid which was crystallized from hot benzene to give 0.48 g (20%) of 4, mp 138-39°.

Anal. Calcd for $C_{10}H_{14}NO_4P$: C, 49.38; H, 5.76; N, 5.76. Found: C, 49.18; H, 5.67; N, 5.58.

IR: ν_{max} (KBr) (cm^{-1}): 1220 (P=O), 1037 (P-O-CH_3), 1000, 925 and 840.

NMR: $\delta_{(CDCl_3)}$: 3.6 (d, J_{P-O-CH_3} = 11 Hz, 6 protons), 3.7 (d, J_{P-CH_2} = 20 Hz, 2 protons) and 7.4 (m, aromatic protons).

MS: m/e - 243.

TLC: Single spot R_f: 0.37 (Benzene:Ethyl acetate, 50:50).

Preparation of 2-Nitrospiro(cyclopropane-1,9'-fluorene) (10)

(i) 2-Nitroethanol:[69] To a stirred suspension of para-formaldehyde (25 g, 0.83 mol) and freshly distilled nitromethane (50 ml) was added in drops 3N methanolic potassium hydroxide until the pH was 8 (~2 ml, 10 min). The reaction mixture became clear in 0.25 hr. After 1 hr additional stirring the reaction mixture was neutralized with 0.2 ml of con. H_2SO_4.

stirred for another hr and the resulting potassium sulphate precipitate filtered and excess nitromethane was freed from filtrate at 40-50° at aspirator vacuum. The golden yellow residue (~60 g) was mixed with an equal weight of diphenyl ether and distilled to give pure 2-nitro ethanol, bp 80°/2-3 mm (lit.[69] 64-66°/0.4 mm), yield 35 g (46%).

IR: ν_{max} (neat (cm^{-1}): 3300 (OH), 2890, 1520 (NO_2 asym.), 1345 (NO_2 sym.) and 1060.

(ii) Nitroethylene:[55] 2-Nitroethanol (10 g, 0.01 mol) and resublimed phthalic anhydride (18 g, 0.1225 mol) was mixed in a distillation apparatus equipped with a short fractionating column and heated using an oil bath. The apparatus was evacuated to 80 mm and temperature maintained at 140-50° until it was hamogeneous. The bath temperature was increased and held at 175-80° until distillation ceased. The distillate was dried over anhydrous $CaCl_2$ and redistilled to give 5.2 g (65%, lit.[55] 5.5 g) of pale yellow lachrymatory oil, bp 39-40°/80 mm.

(iii) 2-Nitrospiro(cyclopropane-1,9'-fluorene):[54] A solution of nitroethylene (2.85 g, 0.04 mol) in sodium dried benzene (25 ml) was added in 0.75 hr to a stirred solution of 9-diazofluorene (7.5 g, 0.04 mol) in dry benzene (75 ml). After 2 minute induction period nitrogen evolution started and the expected volume of nitrogen was collected rapidly. Solvents were removed under reduced pressure at 45-50°, the resulting cake powdered and

dried in vacuum. Crystallization from benzene gave 9.0 g (97%) of 10, mp 110-111°.

Anal: Calcd for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90. Found C, 76.02; H, 4.65; N, 5.82.

IR: ν_{max} (KBr) (cm^{-1}): 1531 (NO_2 asym.), 1351 (NO_2 sym.).

NMR: $\delta_{(CDCl_3)}$: 2.3 (q, anti proton), 2.97 (q, syn.proton), 4.94 (q, t-proton) and 7.4 (m, aromatic protons).

TLC: Single spot R_f: 0.66 (Benzene:Ethyl acetate, 50:50).

Reaction of 2-Nitrospiro(cyclopropane-1,9'-fluorene) with Triisopropylphosphite: Isolation of Cyanomethylene fluorene (12)

Under nitrogen a solution of 10 (1.5 g, 0.006 mol) in freshly distilled triisopropylphosphite (5 ml) was heated at 160-65° for 32 hr. Solvents were removed under reduced pressure and the residue chromatographed over silica gel. Elution with benzene/hexane (80:20) gave 0.45 g of the crude nitrile which on crystallization from benzene/hexane gave 0.42 g (35%) of pure 12, mp 108-109°. This mp was not depressed on admixture with authentic sample mp 108-109° (lit.[56] 110°) whose preparation is described below.

Anal: Calcd for $C_{15}H_9N$: C, 88.6; H, 4.43; N, 6.89. Found: C, 88.35; H, 4.66; N, 6.63.

IR: ν_{max} (KBr) (cm^{-1}) 2203 (C≡N) and 1600 (C=C).

NMR: $\delta_{(CDCl_3)}$: 6.08 (s, olefinic proton) and 7.58 (m, aromatic protons).

TLC: Single spot, R_f: 0.75 (Ethyl acetate).

Preparation of Authentic Cyanomethylene Fluorene (12)[56]:

(i) 9-Cyanomethyl-9-hydroxy fluorene: To a stirred suspension of NaH (1.8 g, 0.07 mol) in dry acetonitrile (1 ml) and dry ether (3-4 ml) was added cautiously fluorenone (1.8 g, 0.01 mol) over a period of 0.25 hr. The suspension was held at room temperature for 20 hr. After the reaction was complete (TLC), about 20 ml of AR methanol was added followed by 3N H_2SO_4 (25 ml). The mixture was extracted with methylene chloride, the organic layer washed successively with water, sodium bicarbonate, water, dried ($MgSO_4$) and solvents evaporated to give a yellow residue mp 104-106°, which on repeated crystallization from benzene/hexane gave 0.41 g (18%) of the nitrile alcohol, mp 109-110° (lit.[56] mp 110°).

Anal. Calcd for $C_{15}H_{11}NO$: C, 81.49; H, 4.93; N, 6.33. Found: C, 81.32; H, 4.86; N, 6.21.

IR: ν_{max} (KBr) (cm^{-1}): 3413 (OH), 2242 (C≡N), 1449, 1361, 1075, 771 and 744.

(ii) Preparation of Cyanomethylene Fluorene (12)[56]: To a stirred suspension of the nitrile alcohol (0.1 g, 0.0005 mol) in glacial acetic acid (1 ml) was added conc. H_2SO_4 (2-3 drops). The resulting mixture was stirred at room temperature for 4 hr and extracted with methylene chloride. The organic layer was washed successively with water, sodium bicarbonate, dried ($MgSO_4$) and solvents evaporated. The residue (mp 93-94°) was chromatographed over silica gel. Elution with benzene/hexane (50:50) gave

nearly pure nitrile (TLC). Crystallization from benzene/hexane gave 0.046 g (50%) of 12, mp 108-109° (lit.[56] mp 110°).

Anal: Calcd for $C_{15}H_9N$: C, 88.66; H, 4.43; N, 6.89. Found: C, 88.40; H, 4.29; N, 6.75.

IR: ν_{max} (KBr) (cm^{-1}): 2205 (C≡N), 1600 (C=C).

Reaction of 9-Diazofluorene with trans-β-Nitrostyrene: Isolation of 2-Nitro-3-phenylspiro(cyclopropane-1,9'-fluorene (11)[57]

A solution of 9-diazofluorene (3 g, 0.015 mol) and trans-β-nitrostyrene (2 g, 0.013 mol) in dry benzene (100 ml) was refluxed for 8 hr. The reaction mixture was freed of solvents under reduced pressure and the crude product crystallized from benzene; yield 3.2 g (65%), mp 173-74° (lit.[57] mp 172°).

IR: ν_{max} (KBr) (cm^{-1}): 1538 (NO_2, asym.) and 1359 (NO_2, sym.).

NMR: $\delta_{(CDCl_3)}$: 4.68 (d, J = 6 Hz, C<u>H</u>-Ph), 5.42 (d, J = 6 Hz, C<u>H</u>NO_2), 6.15 (d, J = 8 Hz, Heavily shielded fluorenyl 8 proton) and 7.4 (m, aromatic protons).

MS: m/e - 313.

TLC: Single spot R_f: 0.70 (Benzene:Ethyl acetate, 50:50).

(A) Reaction of 2-Nitro-3-phenylspiro(cyclopropane-1,9'-fluorene) with Triisopropylphosphite: Isolation of 1,4-Bisfluorenylidine-2,3-diphenyl Butane (15)

Under dry nitrogen a mixture of 11 (2.5 g, 0.0025 mol) and freshly distilled triisopropylphosphite (12 ml) was heated at 145-55° for 24 hr. After the reaction was complete (TLC!),

solvents were removed under vacuum (60-62°/4-5 mm), the residue triturated with petroleum ether (bp 40-60°, 25-30 ml) and filtered. The pale yellow hydrocarbon (mp 205-208°) was crystallized from benzene to give pure 15, mp 230-231°, yield, 0.834 g (39%).

Anal. Calcd for $C_{42}H_{30}$: C, 94.3; H, 5.7. Found: C, 94.57; H, 5.8.

IR: ν_{max} (KBr) (cm^{-1}): 1639, 1592, 1486 and 1435.

NMR: $\delta_{(CDCl_3)}$ (60 MHz): 5.1 (d,t, 2-benzilic protons) and 7.3 (m, aromatic protons); (250 M Hz): 5.12 (J=7 and 2 Hz) and 4.98 (J=7 and 2 Hz).

MS: m/e - 267.

Mol.wt. (Osmometric) - 540.

TLC: Single spot R_f: 0.75 (Benzene:Ethyl acetate, 50:50).

(B) Reaction of 2-Nitro-3-phenylspiro(cyclopropane-1,9'-fluorene) with Triisopropylphosphite: Isolation of Phthalide

Under dry nitrogen a solution of 11 (2.0 g, 0.002 mol) in freshly distilled triisopropylphosphite (10 ml) was heated at 145-155° for 24 hr. Accidental water failure after 16 hr caused the blowing off of solvents by the nitrogen stream. The residue on chromatography over silica gel gave on elution with benzene/hexane (50:50) a crystalline solid mp 76-78°, yield 0.55 g (60%) identified as phthalide by comparison with authentic sample.

Catalytic Hydrogenation of 1,4-bis-Fluorenylidine-2,3-diphenylbutane (15): Isolation of 1,4-bis-Fluorenyl-2,3-diphenylbutane

The hydrocarbon 15 (0.2 g, 0.0004 mol) was hydrogenated in dry THF (120 ml) in presence of 0.025 g of 10% Pd-C in a Parr

hydrogenation apparatus for 13 hr at 40 lb. pressure. Solvents were removed and the residue was chromatographed over silica gel. Elution with benzene gave 0.092 g of 16 which was crystallized from benzene to give 0.077 g (38%) of pure product, mp 250-251°.

Anal. Calcd for $C_{42}H_{34}$: C, 93.66; H, 6.34. Found: C, 93.33; H. 6.47.

IR: ν_{max} (KBr) (cm^{-1}): 1587, 1471, 1430 and 732.

NMR: $\delta_{(CDCl_3)}$: 2.2 (complex multiplet), and 7.2 (m, aromatic protons).

MS: m/e - 538.

Ozonolysis of 15 Involving Oxidative work-up: Isolation of Fluorenone and meso-2,3-Diphenylsuccinic Acid (17)

A solution of 15 in dry methylene chloride (0.2 g, 0.0004 mol, 12 ml) was treated with excess ozone at ~-50° during 1.5 hr. The reaction mixture was left stirred at 0° for one hr and then added to 15 ml of 30% hydrogen peroxide. The mixture was refluxed at 80° for 2 hr, cooled, made basic by addition of sodium carbonate and extracted with methylene chloride. The organic layer was successively washed with water, sodium bicarbonate, water, dried ($MgSO_4$) and evaporated. The residue was chromatographed over silica gel. Elution with benzene/ethyl-acetate (50:50) gave 0.081 g (60%) of fluorenone, mp 82-83°. This mp was not depressed on admixture with authentic sample; further the 2,4-dinitrophenylhydrazone of degradation product was identical (IR) with that of authentic fluorenone 2,4-dinitro-phenylhydrozone.

The aqueous layer on continuous extraction with methylene chloride for 36 hr gave 0.02 g (20%) of a compound, mp 231-233° which was identified as meso-2,3-diphenyl succinic acid on basis of IR, TLC and mp comparison with an authentic sample whose preparation is described below.

Preparation of meso-2,3-Diphenylsuccinic Acid

(i) Benzylcyanide:[70] To a warm solution of powdered sodium cyanide in water (25 g, 25 ml) was added gradually over 0.5 hr, a solution of benzyl chloride in ethanol (45.4 ml, 50 ml). The mixture was heated on a water bath for 4 hr, cooled and the precipitated sodium chloride filtered. The filtrate was concentrated on a water bath and the residual liquid taken in a separatory funnel, the layers separated, the organic layer dried ($MgSO_4$) and distilled bp 100-102°/10 mm (lit.[70] bp 102-103°/10 mm) to give 38 g (95%) of benzylcyanide.

IR: ν_{max} (neat): 2265 (C≡N).

(ii) meso-2,3-Diphenylsuccinonitrile:[59] A stirred warm solution of sodium cyanide in water (15.25 g, 0.3 mol, 25 ml) was diluted with methanol (100 ml) and the mixture heated to gentle reflux. Benzylcyanide (12.5 g, 0.1 mol) was added all atonce, followed by, in drops, over 0.75 hr, a solution of benzaldehyde (13.25 g, 0.125 mol) and benzylcyanide (7.5 g, 0.06 mol). The reaction mixture was stirred at gentle reflux for additional 0.5 hr, cooled, the nitrile collected, washed successively with 40 ml portions of 75% aqueous methanol, water, 75% aqueous

methanol, ether and dried over night. Crystallization from glacial acetic acid followed by washing with 75% methanol, water and ether gave 19 g (65%) of pure meso-2,3-diphenylsuccinonitrile, mp 232-234° (lit.[59] mp 238-239°).

IR: ν_{max} (KBr) (cm^{-1}): 2237 (C≡N), 1504, 1464 and 756.

(iii) meso-2,3-Diphenylsuccinic Acid:[58] A suspension of meso-2,3-diphenylsuccinonitrile (11.7 g, 0.05 mol) in a mixture of conc. sulphuric acid (33.3 ml), water (33.3 ml) and glacial acetic acid (16.6 ml) was refluxed for 11 hr. The resulting grey suspension was diluted with water, filtered and crystallized from acetic acid to give 7.26 g (54%) of meso-2,3-diphenyl-succinic acid (17), mp 222-223° (lit.[58] mp 220°).

IR: ν_{max} (KBr) (cm^{-1}): 3000-2500 (broad), 1709 (C=O), 1393 and 735.

Attempted Characterization of 15 by Degradation

(1) By Oxidation with CrO_3/Ether

To a stirred solution of 15 (0.01 g, 0.00002 mol) in ether (8 ml) was added 0.1 g of chromium trioxide in water (2 ml). No reaction could be observed. (TLC!).

(2) By Oxidation with Potassium Permanganate

A mixture of 15 (0.134 g, 0.00025 mol), potassium permanganate (0.237 g, 0.0015 mol) in acetone (30 ml), acetic acid (0.5 ml) and water (3 ml) was left stirred at room temperature fof 2 hr. No pure products could be obtained on work-up.

3. Ozonolysis followed by Reductive Work-up

A solution of 15 (0.1 g, 0.0002 mol) in dry methylene chloride (10 ml) and pyridine (0.1 ml) was treated with excess ozone at $\sim -50^{\circ}$ for 0.5 hr. The reaction mixture was allowed to attain 0°, treated with zinc dust (0.146 g, 0.002 mol) and glacial acid acid (1.5 ml) and then left stirred at 0° for 2 hr, filtered, the filtrate diluted with water and extracted with methylene chloride. The organic layer was washed successively with sodium bicarbonate, water, dried ($MgSO_4$) and evaporated to give small amounts (0.028 g) of solid, mp 148-150°. Attempted characterization of this material was not successful.

IR: ν_{max} (KBr) (cm^{-1}): 1433, 1188, 1036 and 738.

Preparation of 9-(β-phenyl ethylidiene)fluorene (20)

(i) Phenyl acetyl chloride:[71] Phenyl acetic acid (25 g, 0.175 mol) was heated at 35-40° with thionylchloride (23 g, 0.2 mol) for 25 hr. Excess of thionylchloride was removed at ordinary pressure and the acid chloride distilled, bp 120°/6-8 mm (lit.[71] bp 55-57°/1 mm), yield 18 g (64%).

(ii) 9-(β-phenyl acetyl)fluorene:[60] To a stirred mixture of fluorene (10 g, 0.06 mol) and carbon disulphide (70 ml) was added phenyl acetyl chloride (8 ml) followed by anhydrous $AlCl_3$ (15 g, 0.11 mol) in small portions over a period of 0.5 hr. The mixture was left stirred at room temperature for 24 hr, poured onto crushed ice containing 20 ml of conc. HCl, filtered, washed with water, dried and crystallized from alcohol/benzene

to give 7.30 g (43%) of the ketone, mp 152-154° (lit.[60] mp 155°)

IR: ν_{max} (KBr) (cm^{-1}): 1681 (C=O).

TLC: Single spot R_f: 0.66 (Benzene:Ethyl acetate, 50:50).

(iii) α-(9-fluorenyl)-β-phenyl Ethanol: A solution of the ketone (2 g, 0.006 mol) in THF (15 ml) was introduced in drops over 0.5 hr into a stirred suspension of lithium aluminium hydride (1 g) in dry THF (20 ml). After additional 3 hr stirring the reaction mixture was refluxed for 2 hr, solvents removed under reduced pressure, the residue treated with sulphuric acid (6 N, 25 ml) and extracted with ether (150 ml). The organic layer was washed successively with water, sodium bicarbonate, water, dried ($MgSO_4$) and evaporated. The residue was chromatographed over silica gel. Elution with benzene/hexane (50:50) gave alcohol which on crystallization from a mixture of benzene/alcohol gave 0.896 g (45%) of pure product, mp 138-140°.

IR: ν_{max} (KBr) (cm^{-1}): 3344 (OH), 1053, 775 and 735.

(iv) 9-(β-phenyl ethylidine)fluorene:[61] To a stirred clear solution of the alcohol (0.2 g, 0.0007 mol) in glacial acetic acid (2 ml) was added 15 drops of conc. H_2SO_4. The resulting suspension was stirred at room temperature for 4 hr, diluted with water and extracted with ether. The organic layer was washed successively with water, sodium bicarbonate, dried ($MgSO_4$) and evaporated. The residual pale yellow compound on crystallization from benzene gave 0.148 g (78%) of 20, mp 103-104° (lit.[61], mp 104-106°).

IR: ν_{max}(KBr) (cm^{-1}): 2900, 1587, 1493, 1445, 774 and 735.

TLC: Single spot R_f: 0.76 (Benzene: Ethyl acetate, 50:50).

Reaction of 9-(β-phenyl ethylidine) fluorene with Triisopropyl-phosphite

Under nitrogen atmosphere a solution of 20 (0.05 g, 0.0002 mol) in freshly distilled triisopropylphosphite (1 ml) refluxed for 24 hr. Work-up gave unchanged starting material.

Attempted Dimerization of 20 with Sodium Hydride/Oxygen

A mixture of 20 (0.052 g, 0.0002 mol) and sodium hydride (0.01 g, 0.0005 mol) in dry DMF (2 ml) was heated at 170-180° for 6 hr in presence of oxygen. The reaction mixture was added to water (20 ml), extracted with methylene chloride, the organic layer washed with water and dried ($MgSO_4$). TLC showed no dimer.

Reaction of 2-Nitro-3-phenylspiro(cyclopropane-1,9'-fluorene) with the Carbanion Generated from 9-(β-phenyl ethylidine) fluorene (18)

9-(β-phenyl ethylidine) fluorene (18) (0.026 g, 0.0001 mol) was treated with a suspension of sodium hydride (0.02 g, 0.0001mol) in dry DMF (2 ml). After 0.5 hr, 11 (0.03 g, 0.0001 mol) was added to the stirred mixture. The resulting suspension was heated at 165-170° for 4 hr, cooled, diluted with water and extracted with methylene chloride. The organic layer was washed with water and dried ($MgSO_4$). TLC showed no dimer.

Preparation of o-Nitrostyrene

(i) o-Nitrocinnamaldehyde:[72] To an ice-salt cooled mixture of freshly distilled cinnamaldehyde (55.5 g, 50 ml, 0.42 mol) in acetic anhydride (225 ml) was added, maintaining the inside temperature below 5°, conc. nitric acid (d, 1.42, 18 ml) in glacial acetic acid (50 ml) over a period of 3 hr. The reaction mixture was set aside for 2 days, treated cautiously with dil. hydrochloric acid (20%) and cooled in ice. The light yellow needles of o-nitrocinnamaldehyde were collected, dried. Crystallization from 95% alcohol gave 32 g (43%) of pure material, mp 126-127° (lit.[72] mp 126-127°).

(ii) o-Nitrocinnamic acid:[73] A mixture of onitrocinnamaldehyde (11.0 g, 0.06 mol), hydrogen peroxide (30%, 20 ml) and glacial acetic acid (75 ml) was heated on a steam bath for 50 minutes. The reaction mixture was then cooled and the solid was collected. Recrystallization from aqueous acetic acid gave 7.0 g (58%) of o-nitrocinnamic acid, mp 243-245° (lit.[73] mp 244-246°).

IR: ν_{max} (KBr) (cm^{-1}): 1709 (C=O), 1527 (NO_2, asym.), 1346 (NO_2, sym.), 988, and 760.

(iii) Decarboxylation of o-Nitrocinnamic acid — Preparation of o-Nitrostyrene: An intimate mixture of o-nitrocinnamic acid (5.5 g, 0.028 mol), freshly distilled quinoline (10 ml) and copper powder (0.35 g, 0.005 mol) was heated at 180-185° for 6 hr. The reaction mixture was cooled, neutralized

with dil. hydrochloric acid (3N, 40 ml) and steam distilled to give 0.75 g (18%) of o-nitrostyrene.

IR: ν_{max}(neat): 1690, 1570 (NO_2, asym.), 1310 (NO_2, sym) and 1005.

Reaction of o-Nitrostyrene with Cyclopentadiene: Attempted Isolation of Bicyclo(2,2,1)hept-2(o-nitrophenyl)-5-ene

To an ice-cooled stirred o-nitrostyrene (0.7 g, 0.005 mol) was added freshly cracked cyclopentadiene (0.5 g, 0.0075 mol) and the reaction mixture was left stirred for 1 hr. No reaction (TLC). The reaction mixture was further heated to 45° for additional 1 hr. No further change (TLC).

Preparation of Dibenzalacetone[74]

To a stirred and ice cooled (15-20°) solution of aqueous sodium hydroxide (25 g, 0.625 mol, 200 ml) and alcohol (200 ml) was added a mixture of freshly distilled benzaldehyde (26.5 g, 0.25 mol, 25.5 ml) and AR acetone (7.3 g, 0.13 mol, 9.3 ml). In the beginning one half of the mixture was added over a period of 2-3 minutes. A floculent precipitate formed after 0.25 hr. The remainder of the mixture was added gradually and stirring was continued for additional 0.5 hr. The precipitated solid was filtered, washed with cold water and dried. The crude dibenzalacetone (25 g) was crystallized from ethyl acetate to give 22.5 g (75%) of pure 34, mp 111-112° (lit.[74] mp 112°).

IR: ν_{max}(KBr) (cm^{-1}): 1653 (C=O), 1587, 1342, 1195 and 985.

Reaction of Dibenzalacetone with Triisopropylphosphite: Isolation of bis-Phosphonate (38)

Under nitrogen a stirred solution of dibenzalacetone (2.38 g, 0.01 mol) in distilled triisopropylphosphite (10 ml) was refluxed at 150-160° for 15-16 hr and then left aside at room temperature for a week. The crystalline solid that gradually settled was collected and crystallized from hexane to give 1.82 g (32%) of 38, mp 128-29°.

Anal. Calcd for $C_{29}H_{44}P_2O_7$: C, 61.5; H, 7.77. Found: C, 61.23; H, 7.59.

IR: ν_{max} (KBr) (cm^{-1}): 1724 (C=O), 1250 (P=O) and 992 (P-OiPr).

NMR: $\delta_{(CDCl_3)}$: 0.8 (d, J = 6 Hz, 6 protons, 1-isopropyl-methyl), 1.19, 1.2 (d, J = 6 Hz, 18 protons, 3-isopropyl methyls).

TLC: Single spot R_f: 0.79 (methanol).

Solvents were removed from the filtrate and the residue chromatographed over silica gel. No further pure products could be isolated.

Methandienone: (mp 161-162°) was kindly supplied by CIPLA, Bombay.

IR: ν_{max} (KBr) (cm^{-1}): 3425 (OH), 2915, 1667 (C=O) and 889.

NMR: $\delta_{(CDCl_3)}$: 7.2 (d, β-dienone proton) and 6.25 (m, α-dienone protons).

TLC: Single spot R_f: 0.32 (Benzene:Ethyl acetate, 50:50).

Reaction of Methandienone with Triethylphosphite: Isolation of 41

Under dry nitrogen a solution of methandienone (1.25 g, 0.0037 mol) in sodium dried triethylphosphite (10 ml) was refluxed for 26 hr. Excess of triethylphosphite was removed by distillation (50-60°/8-10 mm) and the crude residue was chromatographed on silica gel. Elution with Benzene:Ethyl-acetate (50:50) gave crude solid (0.975 g) which on crystallization from benzene/hexane (50:50) gave 0.79 g (67%) of 41, mp 130-131°.

Anal: Calcd for $C_{20}H_{26}O$: C, 85.1; H, 9.2. Found:C, 84.64; H, 9.71.

IR: ν_{max} (KBr) (cm^{-1}): 1658 (C=O), 1623, 889 and 820.

NMR: $\delta_{(CDCl_3)}$: 7.2 (d, J = 7 Hz, β-dienone proton), 6.25 (m, α-dienone protons) and 4.7 (broad, olefinic proton).

TLC: Single spot R_f: 0.56 (Benzene:Ethyl acetate,50:50).

Diphenylcyclopropenone[65]

(i) Dibenzyl ketone:[75] A mixture of phenyl acetic acid (35.6 g, 0.262 mol), freshly distilled acetic anhydride (35 ml, 0.35 mol) and fused anhydrous potassium acetate (1.8 g, 0.018 mol) was refluxed for 2 hr in a 250 ml three-necked RB flask fitted with a reflux condenser and a thermometer whose bulb dipped into the liquid. The thermometer registered temperature between 149-150°. The condenser was replaced by a fractionating column and the mixture distilled at atmospheric pressure. The distillation was carried out very slowly, as shown below so that

essentially only acetic acid distilled over.

Time (min.)	Temperature (°C)	
	liquid	vapour
0	145	-
15	146	-
25	149	109
35	151	115
37	152	119
40	154	123
42	161	124
44	165	125
46	171	123
49	190	117
52	204	113

The total distillates consisting of acetic acid and acetic anhydride were collected as a single fraction. Under conditions described above carbon dioxide evolution begins after 0.75 hr. The residue was transfered to a 50 ml RB flask and fractionated under reduced pressure to give phenyl acetone, bp 120-25/25 mm (lit.[75] bp 215-220°), yield 6.5 g (19%) and dibenzyl ketone bp 115-120°/0.35 mm (lit.[75] bp 317-320°), yield 14 g (51%).

(ii) α, α'-Dibromo dibenzyl ketone: To a stirred solution of dibenzyl ketone (10 g, 0.05 mol) in glacial acetic acid (35 ml) was added over 0.25 hr, a solution of bromine in acetic acid (16 g, 50 ml, 0.1 mol). The mixture was left stirred for

additional 5 min. and then poured into water (125 ml) and treated with solid sodium bisulphite till the yellow colour of the solution was discharged. The mixture was allowed to stand for 1 hr, filtered and air dried. Recrystallization from benzene/hexane (50:50) gave 13 g (74%) of the dibromo compound, mp 78-93° (lit.[65] mp 79-97°).

(iii) Diphenylcyclopropenone:[65] To a stirred dry methylene chloride solution of α, α'-dibromo dibenzyl ketone (10.8 g, 0.03 mol, 50 ml) was added freshly distilled triethylamine (10 ml) over a period of one hr. The mixture was left stirred for additional 0.5 hr, treated with 3N HCl (2 x 20 ml) and the organic phase was transfered to a flask and cooled in an ice-bath. To the stirred solution was added cold sulphuric acid (5 ml in 3 ml of water) slowly. The slightly pink precipitate of diphenylcyclopropenone bisulphate that separated was filtered, washed with methylene chloride (20 ml) and to a stirred suspension of the adduct in methylene chloride, water (30:50, 80 ml) was added solid sodium carbonate (0.5 g) in small portions. The organic layer was separated, washed with water, dried ($MgSO_4$) and evaporated. The impure diphenylcyclopropenone (3.1 g) on repeated crystallization from boiling cyclohexane gave pure compound 2.8 g (47%), mp 118-120° (lit.[65] mp 119-120°).

Anal: Calcd for $C_{15}H_{10}O$: C, 87.37; H, 4.85. Found: C, 87.21; H, 4.63.

IR: ν_{max} (KBr) (cm^{-1}): 1838, 1613, 1449 and 767.

TLC: Single spot R_f: 0.74 (Methanol).

Reaction of Diphenylcyclopropenone with Triisopropyl phosphite: Isolation of isopropyl α-Phenylcinnamate (44)

Under nitrogen a solution of diphenylcyclopropenone (0.2 g, 0.001 mol) in distilled triisopropylphosphite (1 ml) was left stirred at room temperature for 20 hr. TLC showed complete absence of starting ketone. Solvents were removed in vacuuo and the resulting crude sample was chromatographed over neutral alumina. Elution with hexane gave a colourless compound which on dissolution in hot hexane and cooling gave 0.090 g (35%) of 44, mp 63-65°. The sublimed material melted at 72-73°.

Anal: Calcd for $C_{18}H_{18}O_2$: C, 81.96; H, 6.76. Found: C, 81.90; H, 6.65.

IR: ν_{max} (KBr) (cm^{-1}): 1695 (C=O).

PMR: $\delta_{(CDCl_3)}$: 1.3 (d, J = 6 Hz, 6 protons, i-Pr), 5.3 (heptet, 1 proton), 7.3 (m, 10 aromatic protons) and 8.0 (s, olefinic proton).

MS: m/e - 266.

TLC: Single spot R_f: 0.68 (Benzene:Ethyl acetate, 50:50).

Reaction of Diphenylcyclopropenone with Isopropanol at Room Temperature

Diphenylcyclopropenone (0.041 g, 0.0002 mol) was stirred at room temperature along with isopropanol (2 ml) for 22 hr. TLC showed no change. Removal of solvents resulted in the complete recovery of the starting material.

Preparation of 3-Bromophthalide[77]

(i) Phthalide:[76] To a stirred thick paste of zinc dust (36 g, 0.55 mol), copper sulphate (0.2 g, 0.0013 mol), water (8 ml) and aqueous sodium hydroxide (80 g, 2 mol, 65 ml) was added under cooling phthalimide (29.4 g, 0.2 mol) over 0.5 hr. Stirring was continued for additional 0.5 hr. The mixture was diluted with water(30 ml), warmed on a steam bath until evolution of ammonia ceased, concentrated to 80 ml under reduced pressure, cooled and filtered. The filtrate was made acidic with conc. hydrochloric acid (30 ml). The oily layer that separated on cooling solidified to a hard reddish brown cake. The crude material was crystallized from hot water to give 16.5 g (61%) of phthalide, mp 71-72° (lit.[76] mp 72-73).

IR: ν_{max} (KBr) (cm^{-1}): 1724 (C=O), 1276, 1211, 1047 and 998.

(ii) 3-Bromophthalide:[77] Under illumination from a 100 watt bulb a mixture of phthalide (10 g, 0.075 mol), N-bromosuccinimide (13.3 g, 0.075 mol) and dry carbon tetrachloride (200 ml) was refluxed for 0.5 hr. The end of the reaction was indicated by the disappearance of N-bromosuccinimide from the bottom of the flask and accumulation of succinimide at the top of the reaction mixture. The succinimide was removed by filtration and the filtrate was concentrated to 15-20 ml, cooled and filtered to give 12 g (75%) of crude 3-bromophthalide, mp 74-80°. Crystallization from cyclohexane gave 10.9 g (68%) of almost

colourless plates, mp. 78-80° (lit.[77] mp 78-80°).

IR: ν_{max} (KBr) (cm^{-1}): 1795, 1471, 1282, 1042 and 985.

Reaction of 3-Bromophthalide with Triisopropylphosphite: Isolation of 3-(o-methyl benzoyl)phthalide (46)

A benzene solution of 3-bromophthalide (1 g, 0.005 mol, 3 ml) was treated with freshly distilled triisopropylphosphite (2.5 ml) and the solution left stirred at 80-90° for 36 hr. Concentration and cooling led to deposition of white crystals (0.095 g, 16%) of 46, mp 138-40°. Crystallization from benzene gave almost colourless shining crystals, mp 157-158°.

Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.15; H, 4.76. Found: C, 75.74; H, 5.25.

IR: ν_{max} (KBr) (cm^{-1}): 1767 (C=O)

NMR: $\delta_{(CDCl_3)}$: 2.65 (s, aromatic methyl), 6.9 (s, t-proton), and 7.5 (m, aromatic protons).

TLC: Single spot R_f: 0.64 (Benzene:Ethyl acetate, 50:50).

Reaction of 3-Bromophthalide with Triisopropylphosphite under reflux

3-Bromophthalide (1 g, 0.005 mol) in distilled triisopropylphosphite (10 ml) was refluxed under nitrogen at 140-150° for 72 hr. Excess of the reagent was removed under reduced pressure (65-75°/8-10 mm) and the residue was chromatographed over silica gel. Elution with benzene/ethyl acetate (50:50) gave

0.052 g of a compound, mp 281-282° which has not yet been fully characterized.

Anal. Found: C, 72.19; H, 3.94.

IR: ν_{max} (KBr) (cm^{-1}): 3520 (OH), 1750 (C=O).

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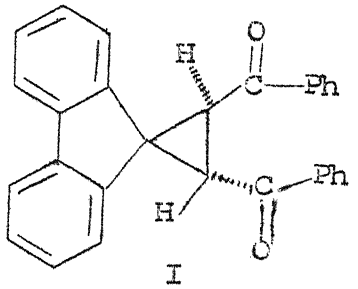
III. REACTIONS OF 2,3-DIBENZOYLSPIRO(CYCLOPROPANE-1,9'-FLUORENE) — A REEXAMINATION

III.A INTRODUCTION

In terms of reactivity expected from cyclopropanes to which electrophilic functions are attached, nitrocyclopropanes (Chapter II) and cyclopropane carbonyl compounds can be expected to exhibit much versatility in their reactions. This is indeed so!

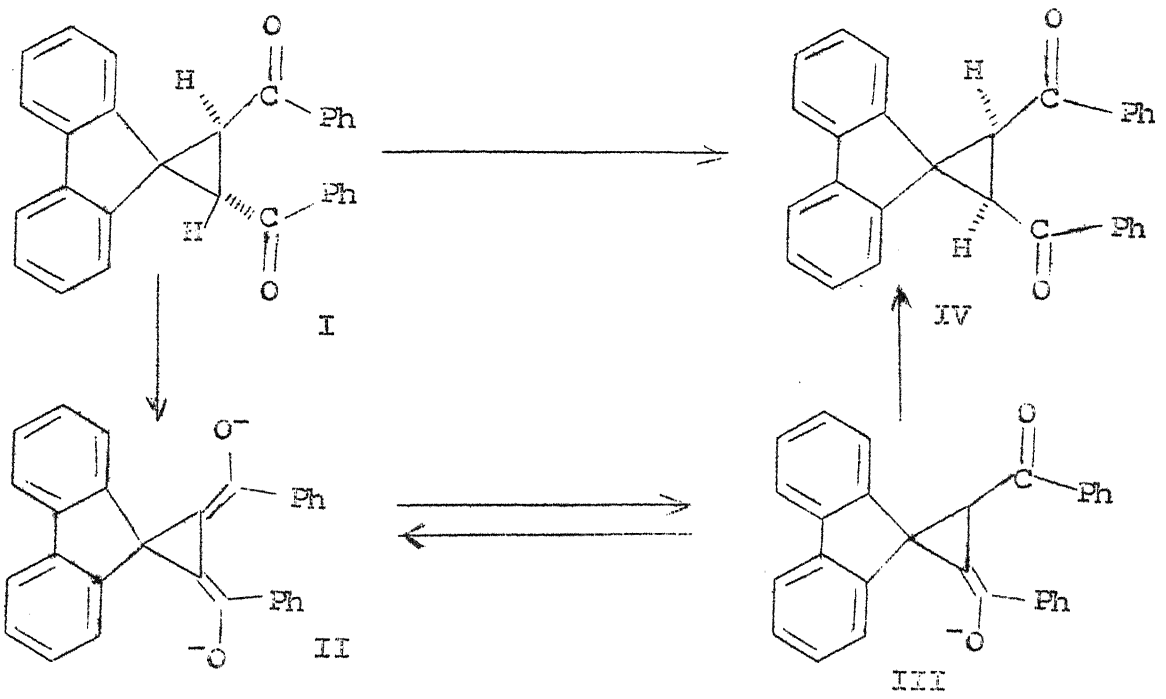
The present work is an attempt to understand the rather unique transformations reported with I:



I

Cyclopropane I was reported to undergo various transformations which were not understood and which led to crystalline products of unknown structures.[1] Of special interest is reaction of I with hot excess methanolic potassium hydroxide to form a red potassium salt, tentatively designated as the dipotassium derivative of dienolate II, which upon treatment with methanolic hydrogen chloride gave a yellow isomer melting at 195°.[1] This product, unlike I, was oxidized by potassium permanganate in acetone and yielded an inner azine readily on treatment with hydrazine hydrate.[1] Finally reduction of I, as well as the 195° melting material with zinc and acetic acid gave same compound melting at 209°.[1]

Although the initial workers[1] did not designate a specific structure for the product melting at 195°, Chemical Abstracts has designated it as cis-1,2-dibenzoylspiro(cyclopropane-1,9'-fluorene) IV.[2]



The I → IV change under these conditions, if true, although mechanistically plausible, should be considered unusual in that the key intermediate III should be expected to exhibit great propensity for ring rupture. Consequently it was felt that the changes involving I should be of a more complex nature and the investigations presented in Section C bear this out.

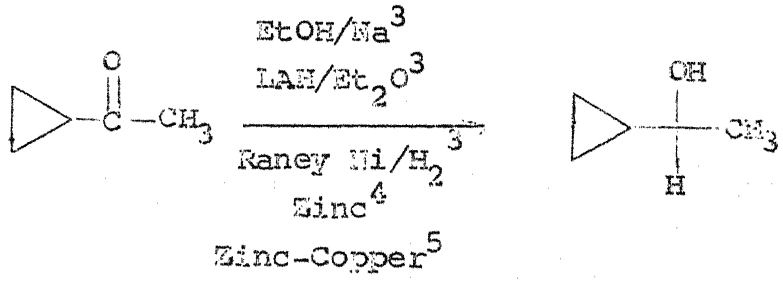
In the following section the transformation of cyclopropane carbonyl compounds are presented to provide a proper back ground.

III.B BACKGROUND

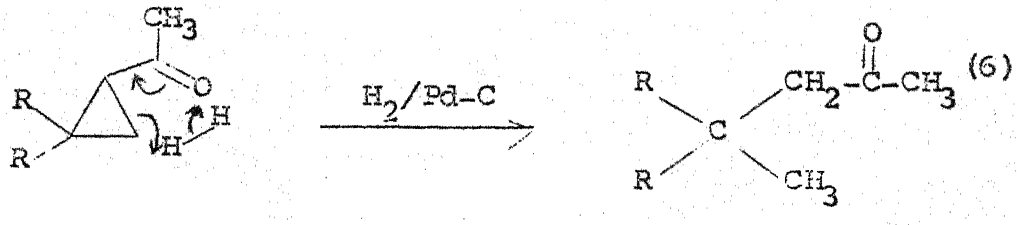
The cyclopropane carbonyl system has been investigated in some detail and many novel transformations involving these compounds have been reported. Of special interest is the current activity in this area involving the use of this substrate to demonstrate facets of concerted processes. No review has appeared on the reaction of cyclopropane carbonyl compounds and consequently the following critical compilation should be useful.

Transformation of Cyclopropane Carbonyl Compounds Initiated by Reducing Agents:

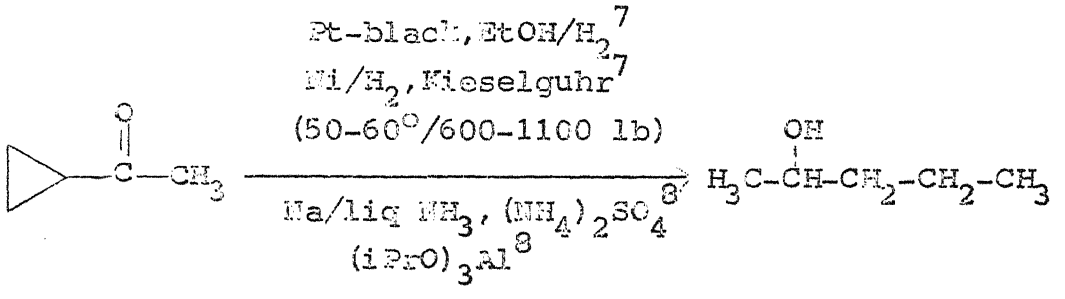
The choice of the reducing agent makes possible the reduction of cyclopropyl ketones either to the corresponding carbinols or to ketones arising from hydrogenolysis of the cyclopropane ring or to alcohols arising from these ketones.



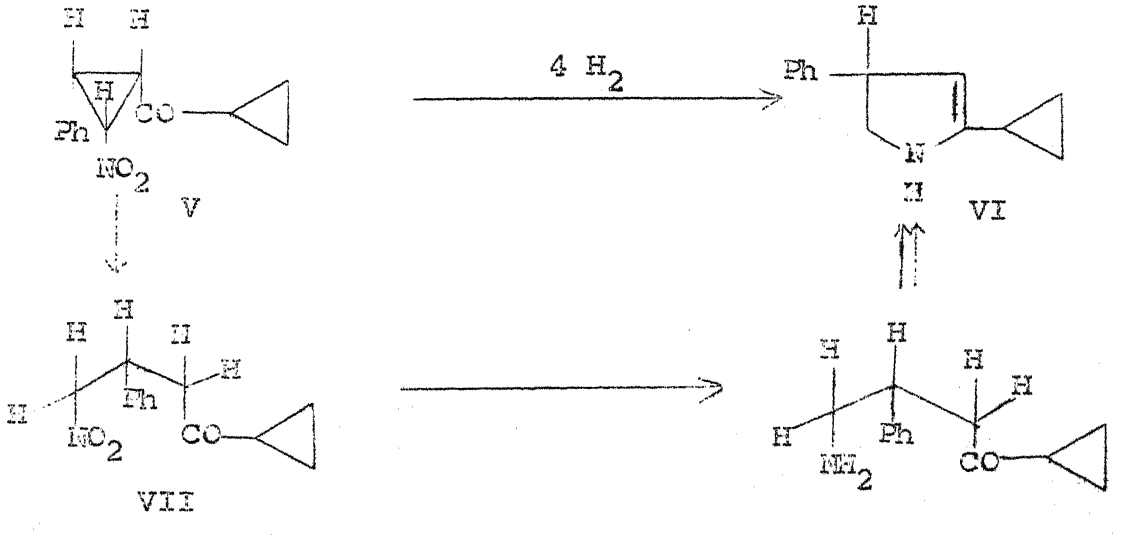
The transformation of cycloproyl ketones to the corresponding open chain analogous can be best explained on the basis of a 1,4-addition of hydrogen:



The carbonyl compounds thus formed can undergo further reduction:



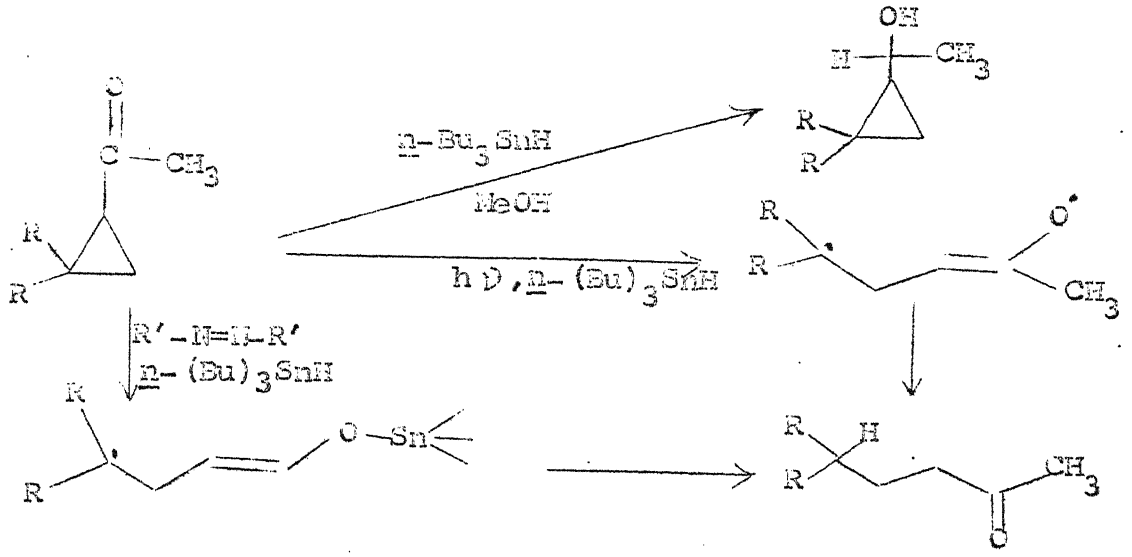
The tendency for ring rupture can be enhanced by additional electron withdrawing groups and is illustrated by the following:[9]



In accordance with the suggested mechanism, VII could be transformed to VI under the reaction conditions.

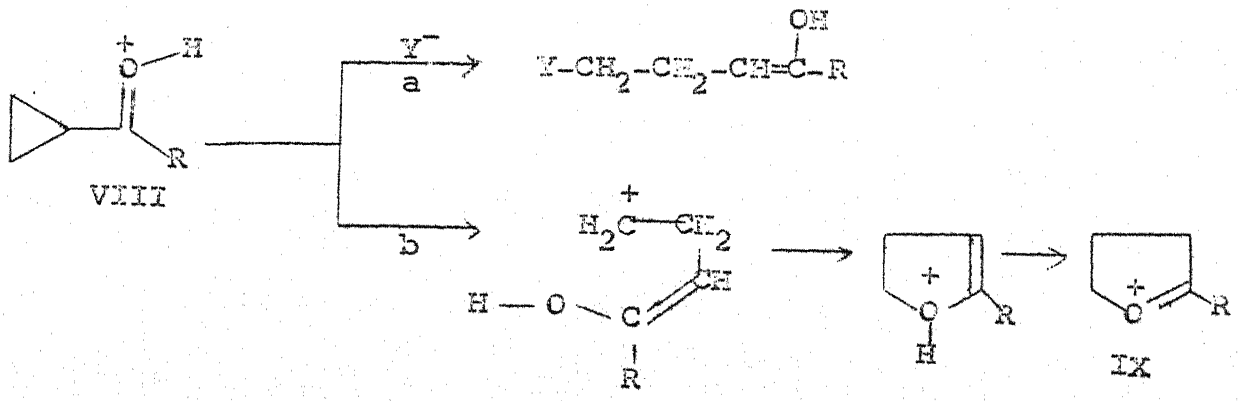
It has been shown recently[10] that the normal course of $n\text{-}Bu_3SnH$ action involving the formation of cyclopropyl carbinols can be changed photochemically or in the presence of radical

initiators to yield ketones arising from ring rupture:

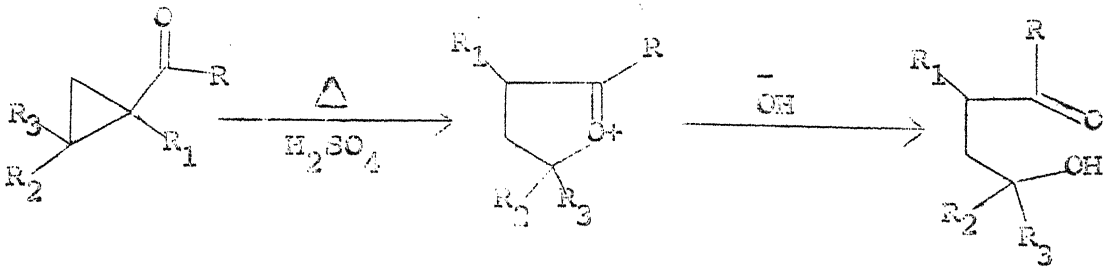


Transformations Initiated by Electrophiles:

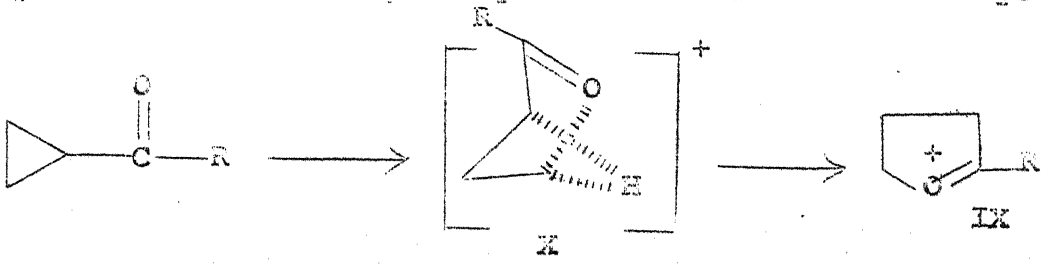
The rupture of the cyclopropane ring arising from acceptance of the electrophiles by the carbonyl oxygen is the primary pathway in reactions involving cyclopropane carbonyl compounds. Where protons are the electrophilic species, further changes of the protonated cyclopropane VIII can take place either by direct attack of an external nucleophile (path-a) or through intermediate IX arising from intra-molecular participation of the oxygen function: (path-b)



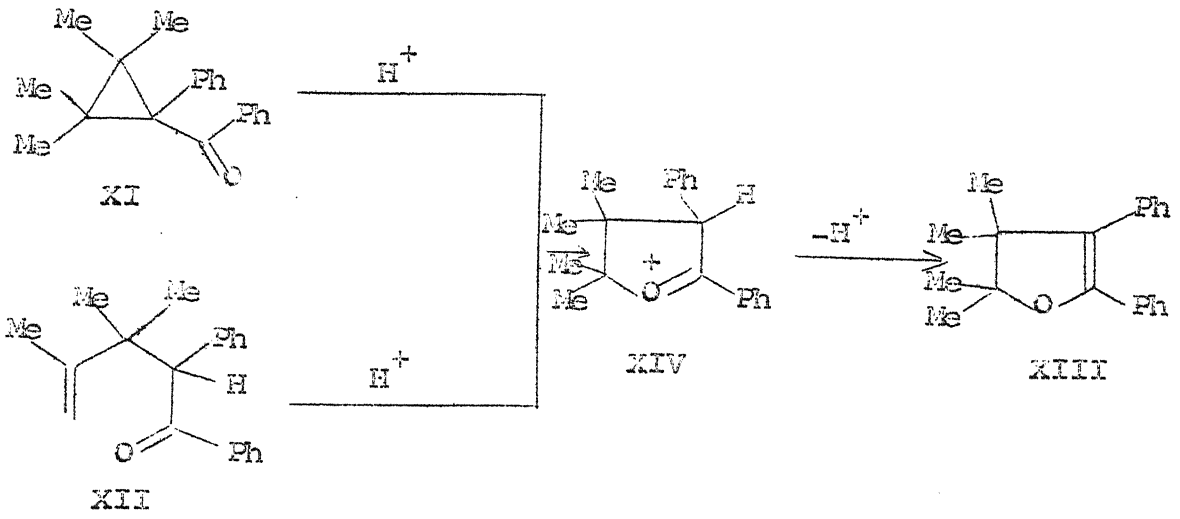
Indeed several compounds belonging to system IX have been recently identified through NMR and these were made *in situ* by warming the appropriate precursor in sulphuric acid:[11]



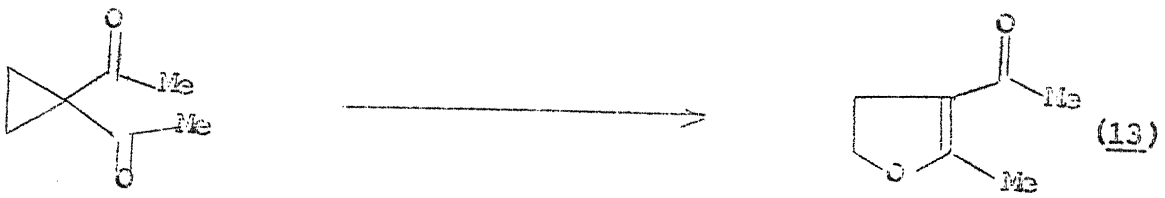
The cations can be quenched with alkali to yield the expected ω-hydroxy ketones. Species IX can also arise through the O-protonated intermediate X; however in view of the known quantitative transformation of cyclopropyl ketones to VIII with acids and the total inertness of 2-nitro 2-phenyl benzoyl cyclopropane to acids this pathway is considered less likely.



As expected ions represented by IX can be readily transformed to dihydrofurans by loss of proton from 3-position. This is an important pathway, particularly when substituted cyclopropanes are involved. The experimental observation[12] that XIII could be obtained from XI and XII with acid strongly supports involvement of ion XIV as a common intermediate:



Further interesting examples belonging to this category are:



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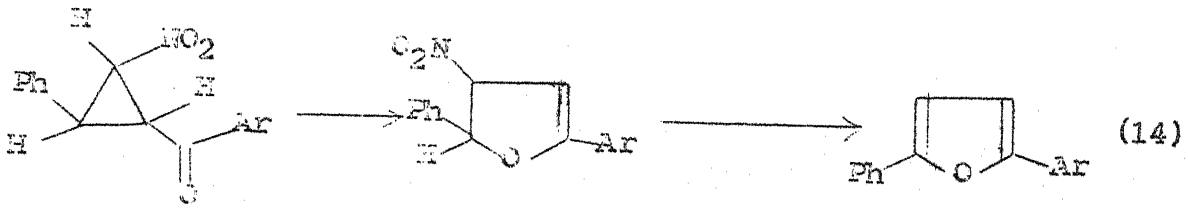

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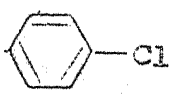
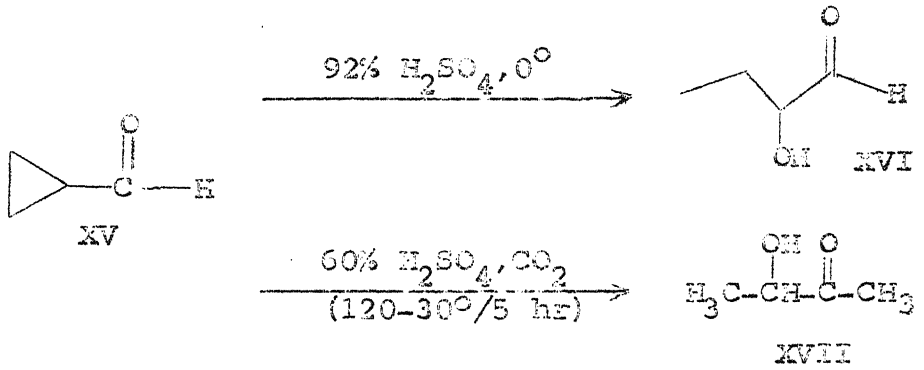
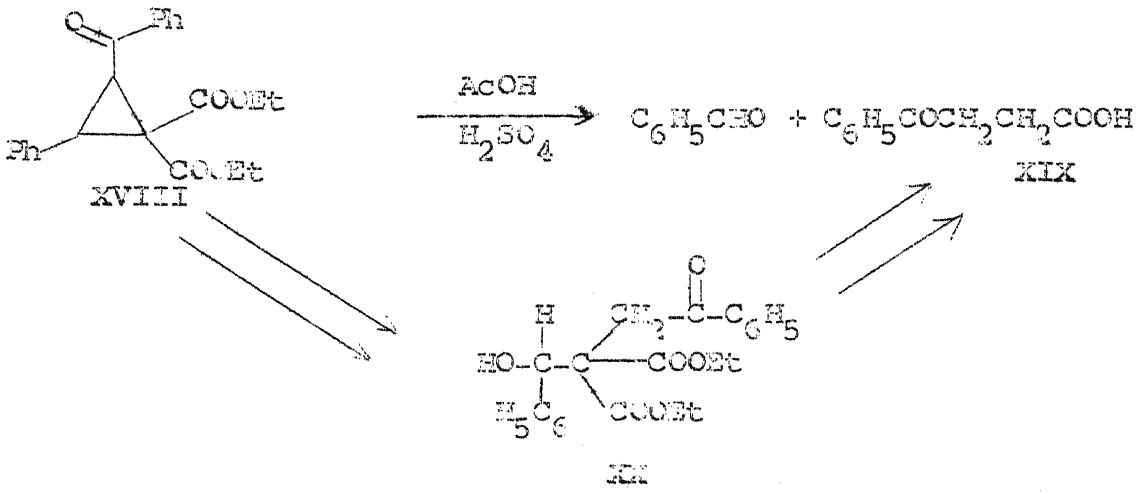
Ar = 

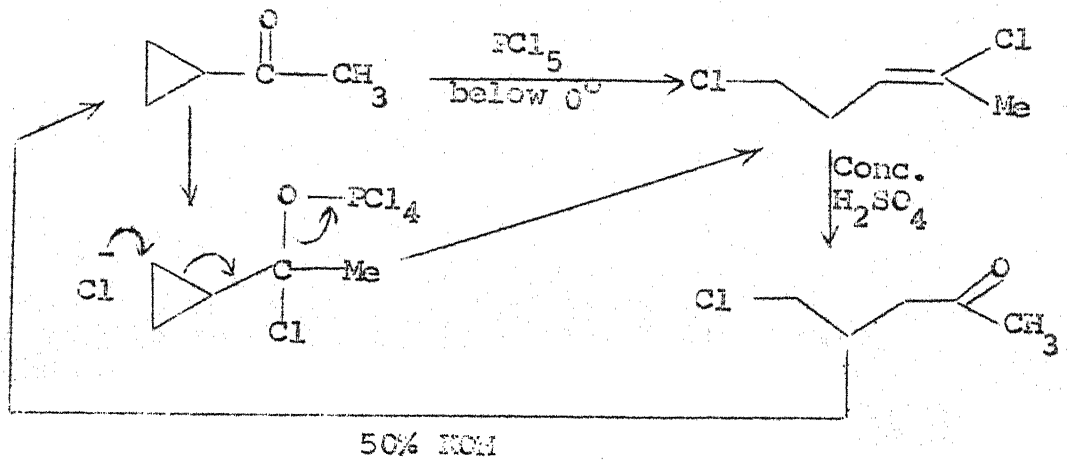
In this context the reported[15] sulphuric acid induced transformation of the parent system cyclopropane-1-carboxaldehyde (XV) to α-hydroxy butyraldehyde (XVI) and acetoin (XVII) are most perplexing and merit reexamination:



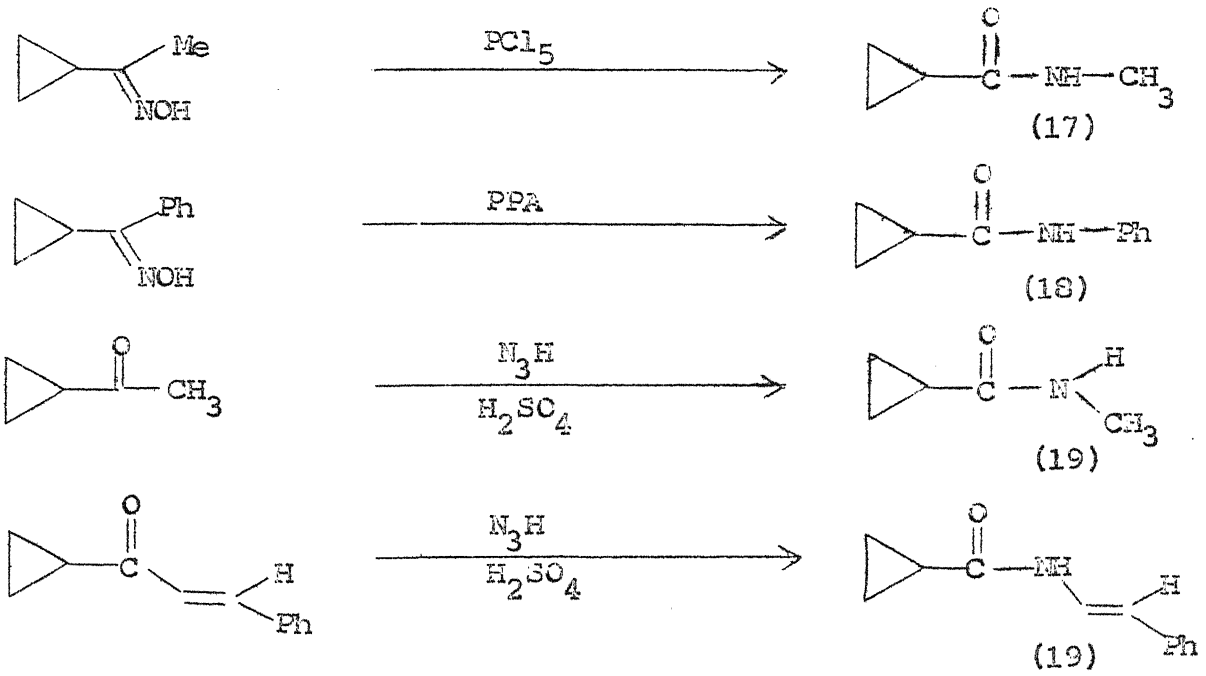
Benzoyl cyclopropane gives the expected ω-acetoxy propyl phenyl ketone and finally the cyclopropane XVIII gives acid XIX through fragmentation of the ω-hydroxy intermediate XX[14]:



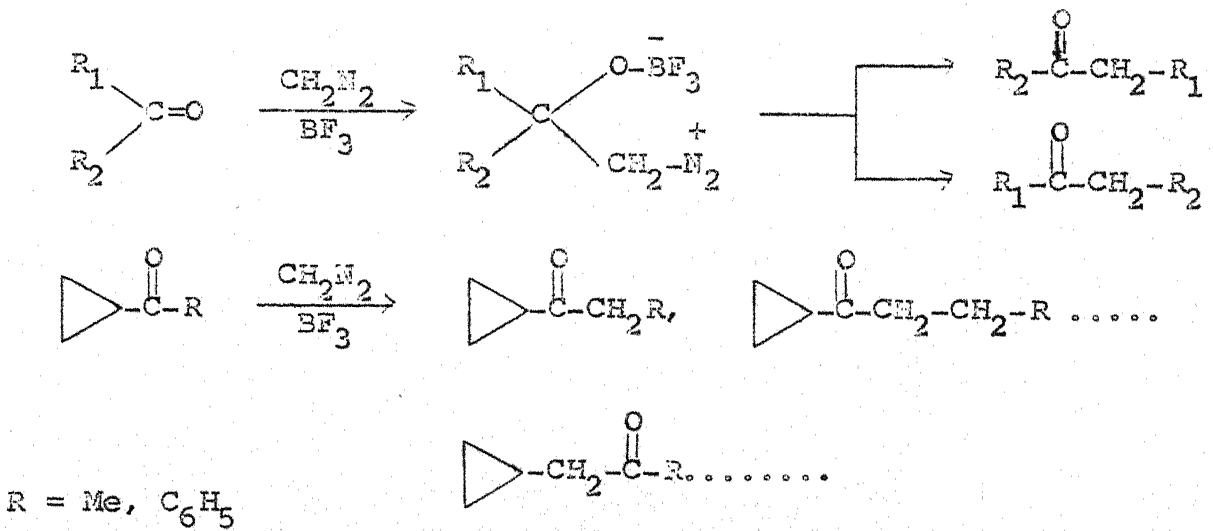
The transformation of cyclopropyl methyl ketone to 2,5-dichloro-2-pentene[16] can be rationalized on basis similar to pathway a:



In Beckmann rearrangements either involving the cyclopropyl ketoximes with electrophiles or cyclopropyl ketones with hydrazoic acid, the cyclopropane ring as expected does not migrate:

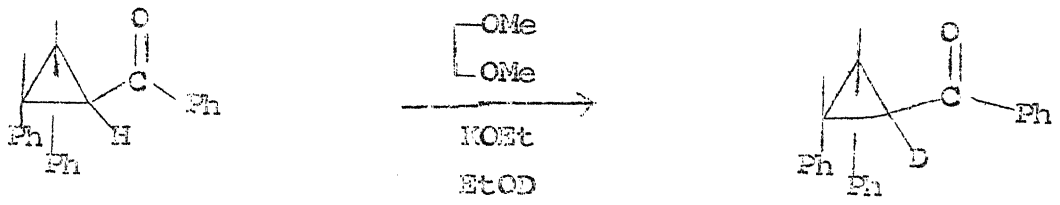


The reaction of cyclopropyl ketones with diazomethane take place by pathway indicated below and show little discrimination[20]:

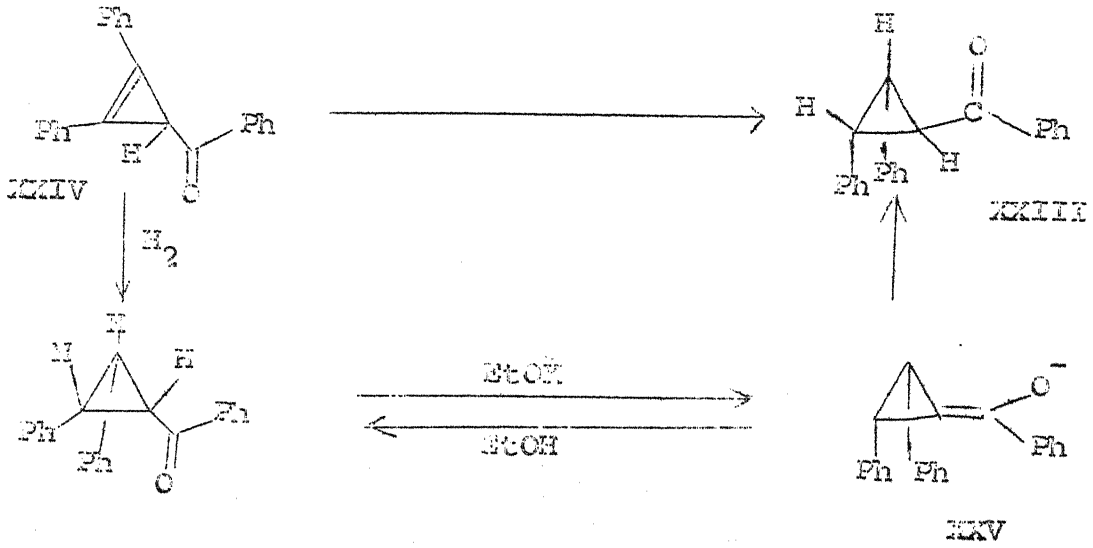


R = Me, C_6H_5

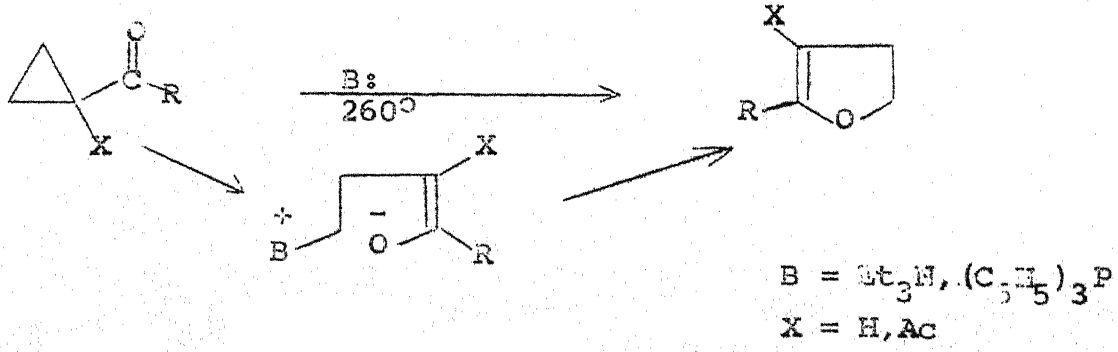
It is interesting to note that the deuterium exchange takes place with retention of configuration in (XXIII):



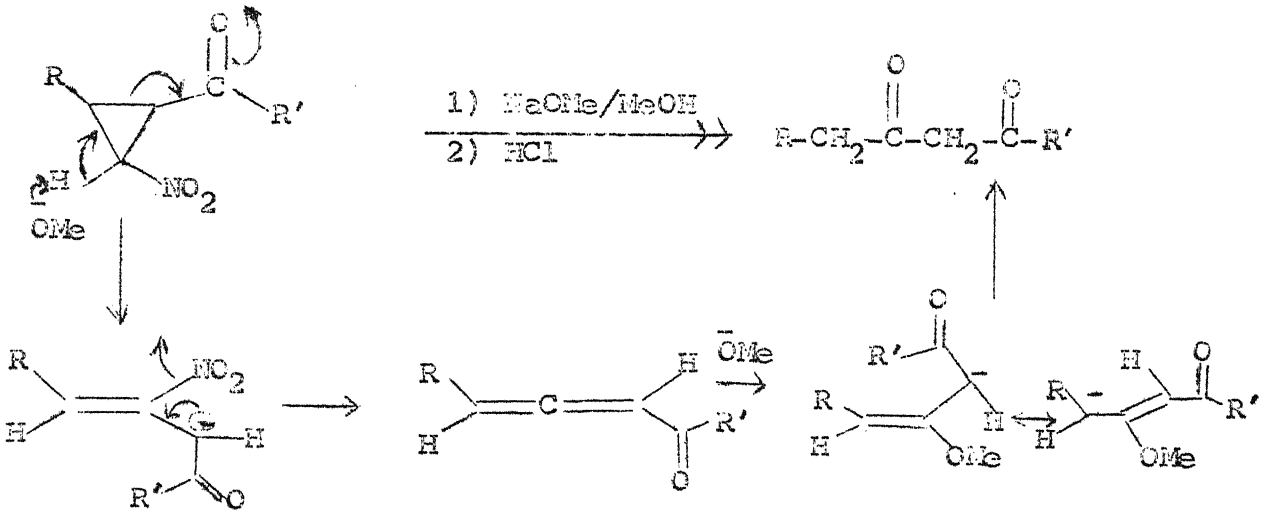
However, in the preparation of XXIII from XXIV involving a sequence of hydrogenation and equilibration, the planar anion XXV is implicated:



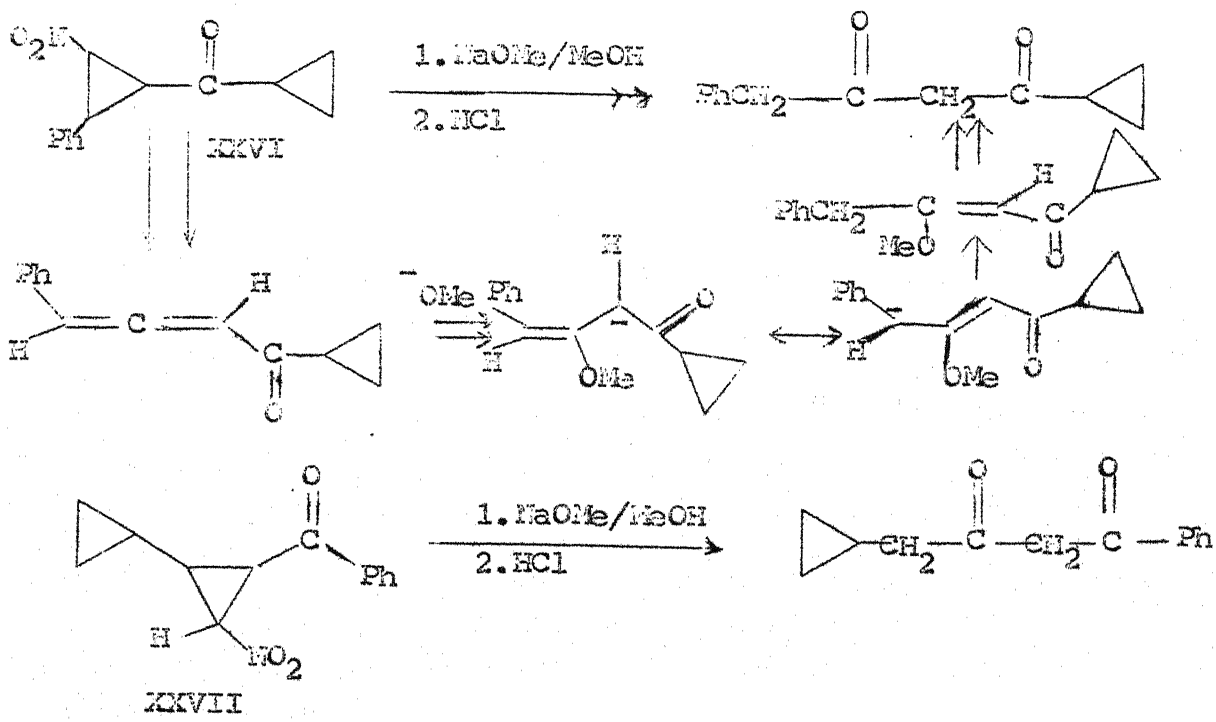
The Michael-equivalent with the cyclopropyl carbonyl compounds can be realized with either tertiary bases or triphenyl phosphine to give 4,5-dihydrofurans.[24]



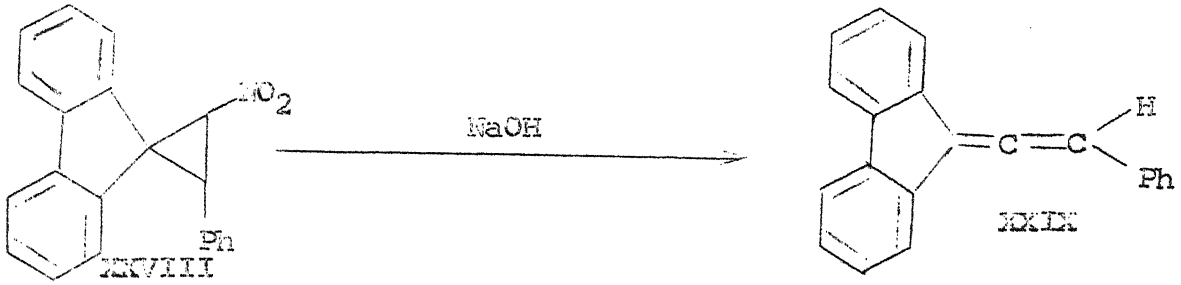
Nitrocyclopropyl ketones undergo facile ring rupture with bases to give the corresponding enolates. The reaction generally proceeds further to give product where the nitro function gets replaced.[25] We would like to explain these changes on basis of an allene intermediate:



Variations of this reaction are exemplified involving XXVI and its isomer XXVII.[26]



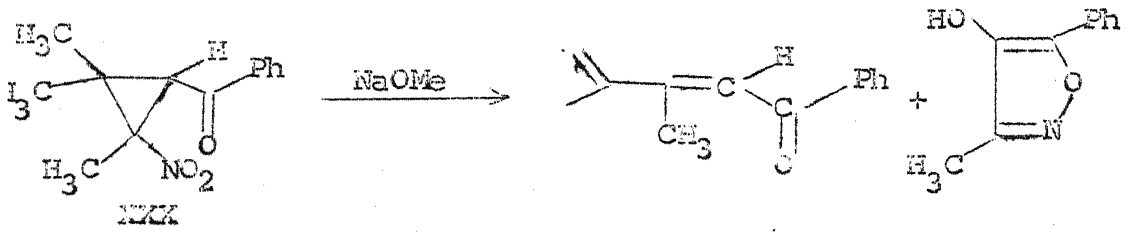
The proposed intermediacy of an allene derives support from the reported transformation of XXVIII to allene intermediate XXIX[27]:



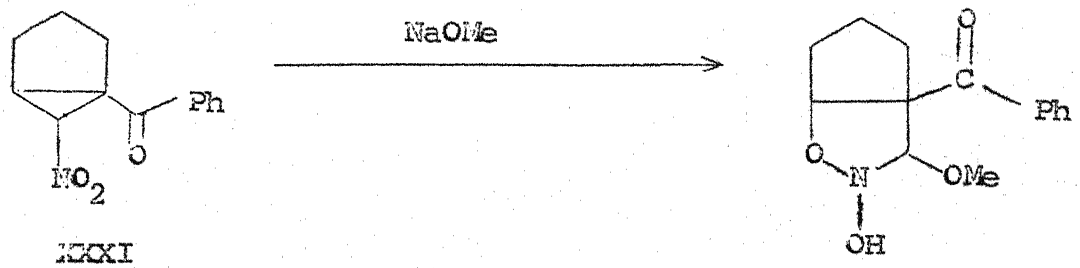
XXVIII XXIX

Alternate possibilities include a direct displacement with methoxide or an addition-elimination process from the initially formed ring ruptured product.

The transformations of cyclopropyl ketones XXX and XXXI are much more complex[28,29] and perhaps the product structural assignments should be further scrutinized:

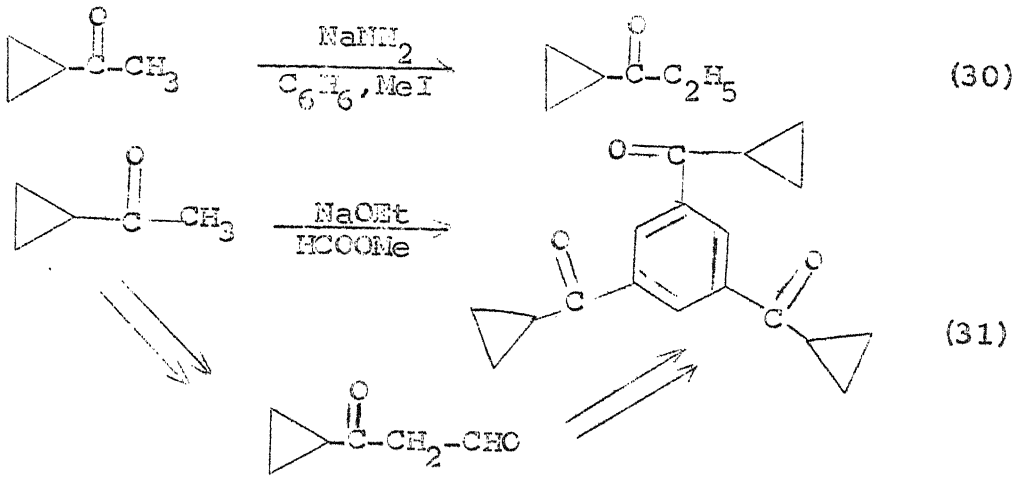


XXX



XXXI

Cyclopropyl methyl ketones in presence of base undergo exclusive alkylation, acylation and halogenation at the alkylsite:



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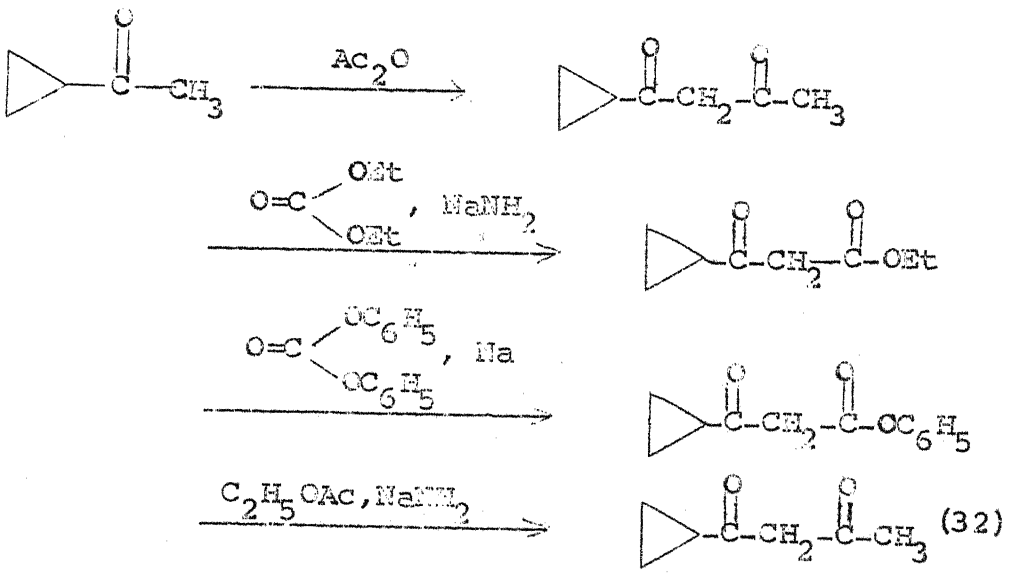
(31)



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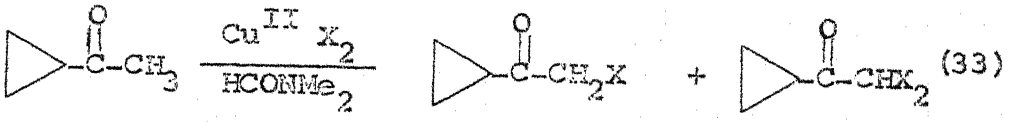
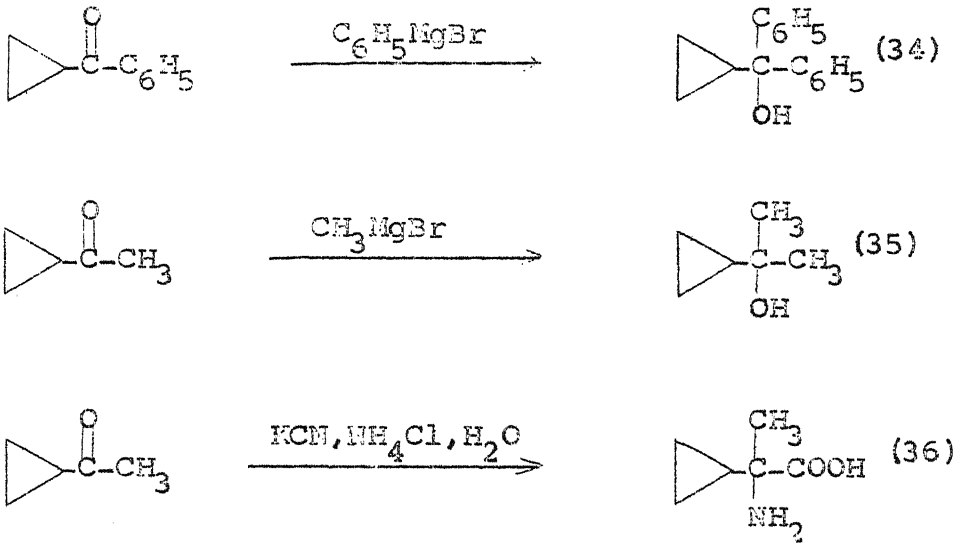


(33)

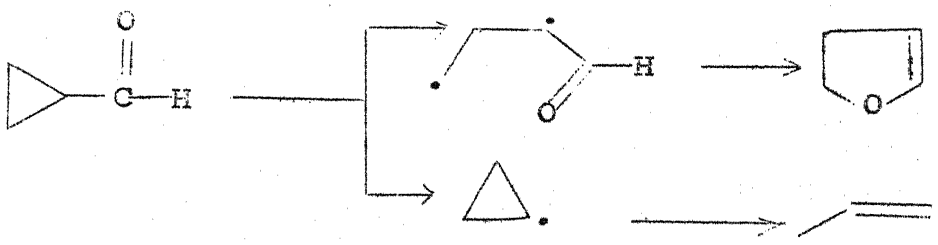
X = Cl, Br

Nucleophiles add to the carbonyl function of cyclopropyl ketones without complication:



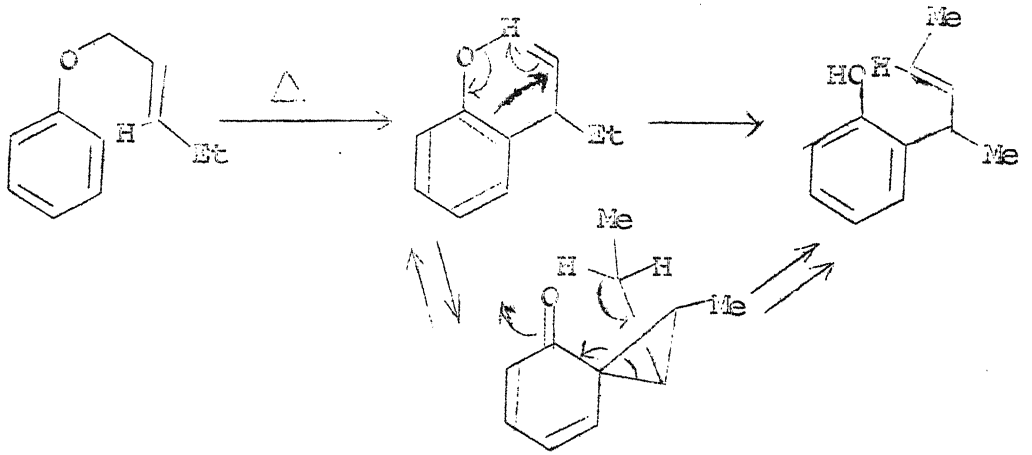
Thermal Transformations:

At 500° cyclopropane carboxaldehyde is transformed to 4,5-dihydrofuran and propylene.[37] The formation of these products could be rationalized on basis of radical intermediates:

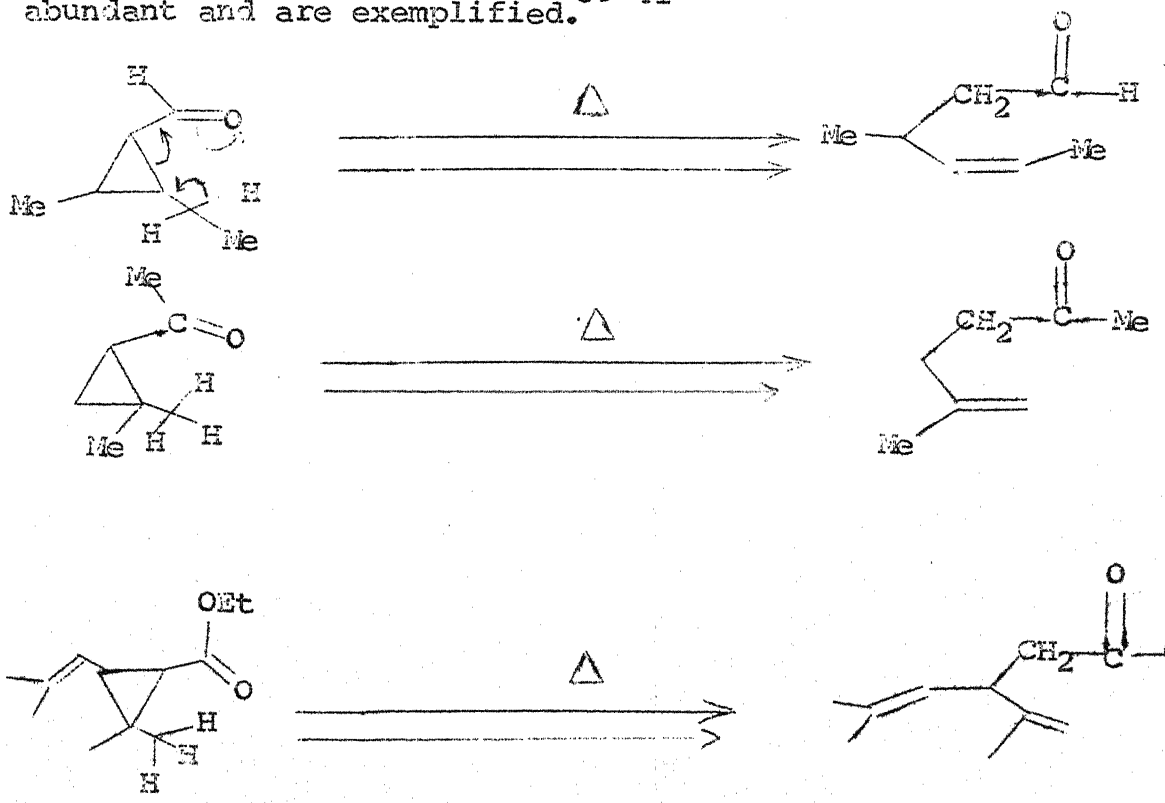


The more interesting transformations of this category are those where the cyclopropyl sigma bond participates in concerted

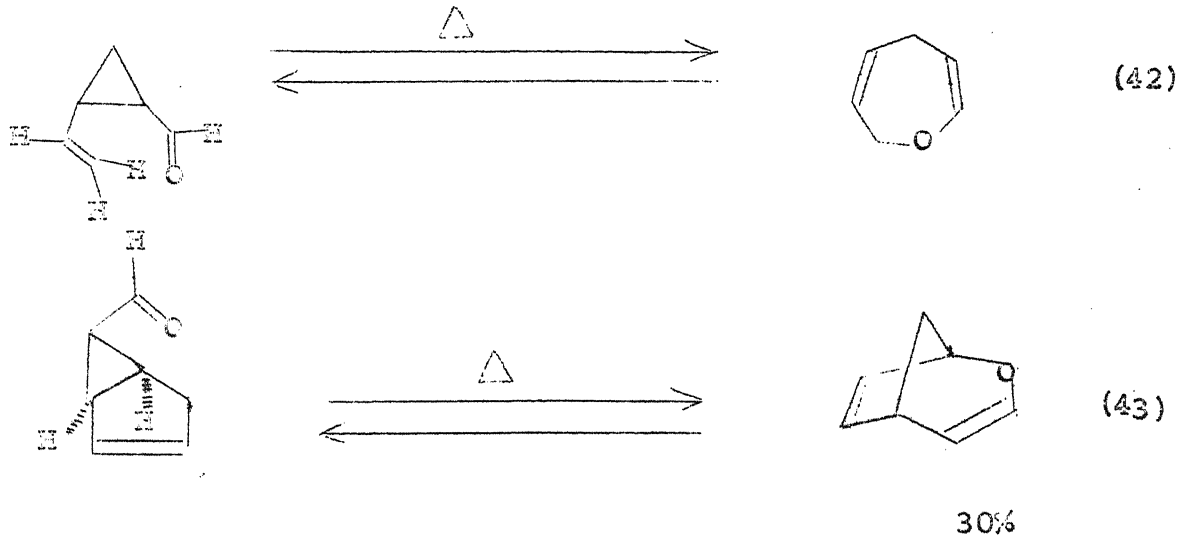
processes. The most well known example of this class is the abnormal Claisen rearrangement:[38]



The mechanistic pathway proposed above has been verified by labelling experiments and is definitely a concerted process. Variations of this rearrangement are becoming increasingly abundant and are exemplified.[39-41]



Examples of 3,3-sigmatropic shifts involving the cyclopropyl carbonyl function have been reported recently:[42,43]



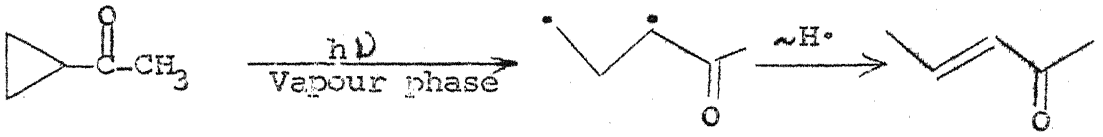
(42)

(43)

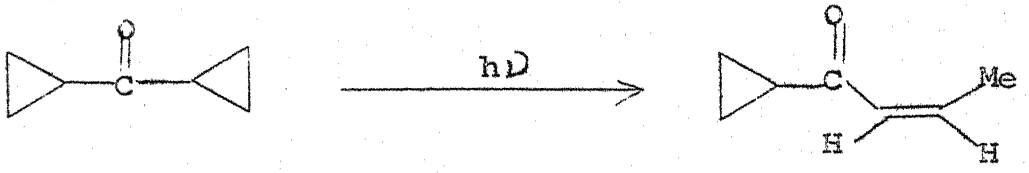
30%

Photochemical Transformations:

Cyclopropyl carbonyl compounds either undergo ring rupture or isomerization or rearrangement on photolysis. Cyclopropyl methyl ketone gives 2-pentene-4-one involving a diradical intermediate:[44]

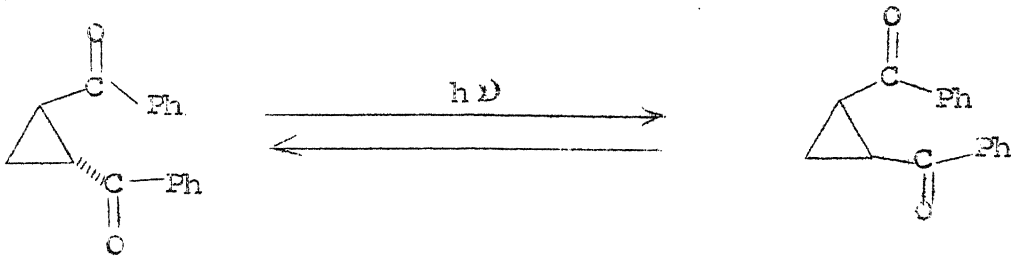


Similarly dicyclopropyl ketone gives XXXII:[45]

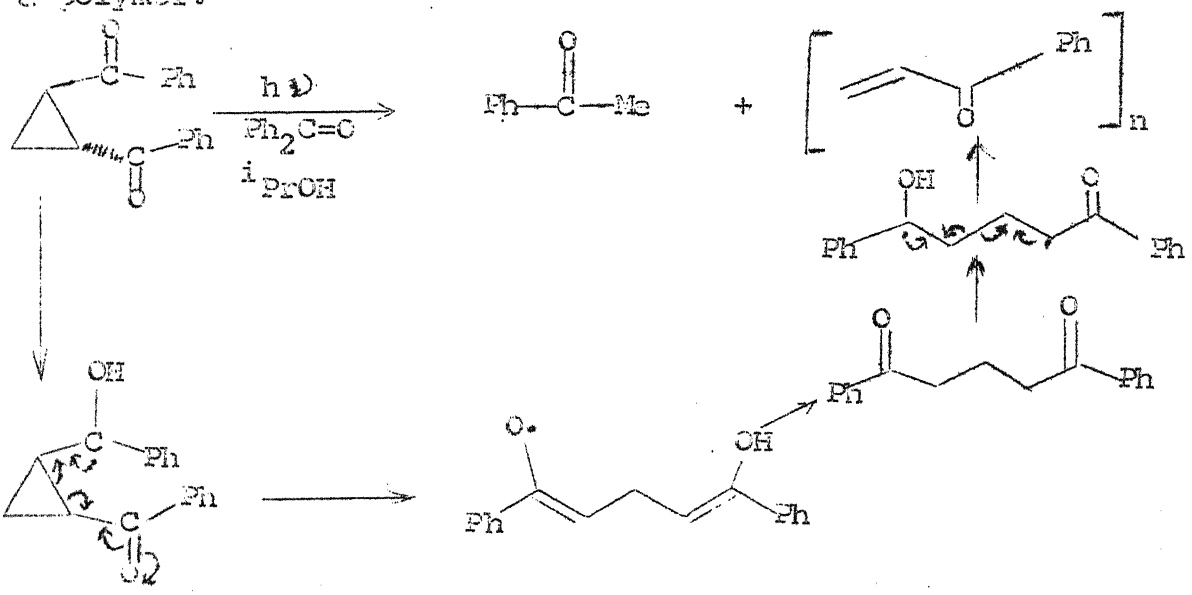


XXXII

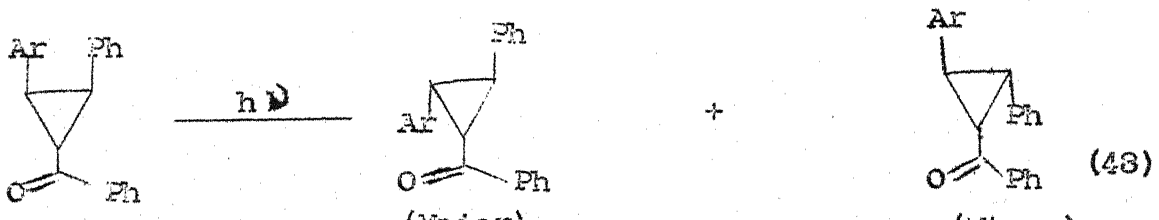
1,2-Dibenzoyl cyclopropanes give rise to a photostationary state:[46,47]



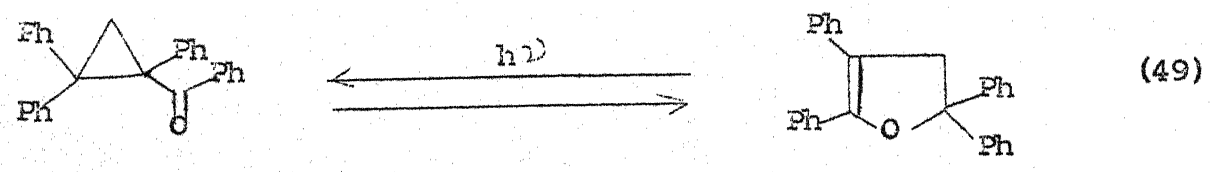
However, in presence of a sensitiser and a hydrogen donor solvent trans-1,2-dibenzoyl cyclopropane is transformed into acetophenone and a polymer:[46]



Heavily substituted benzoyl cyclopropanes either yield isomers or undergo transformations to dihydrofurans:[48,49]

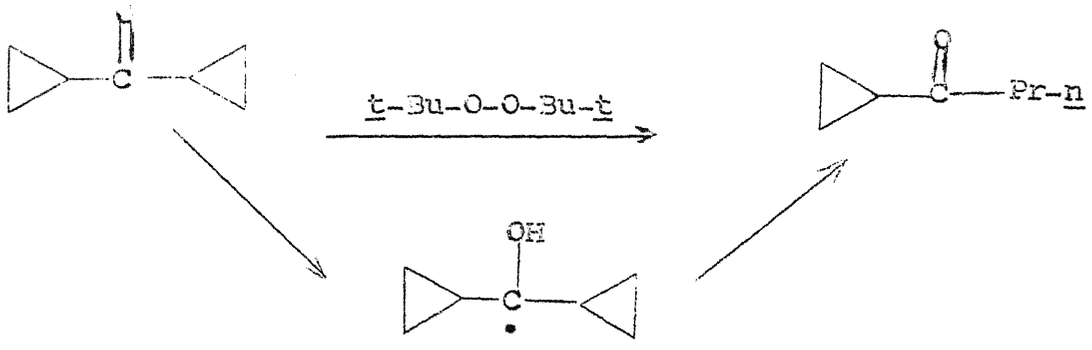


(48)



(49)

Closely related to photochemical transformations is the dicyclopropyl ketone to n-propyl cyclopropyl ketone change:[50]



III.C PRESENT WORK

Abstract

The reported rather unique transformations leading to unknown products, of system trans-2,3-dibenzoylspiro(cyclopropane-1,9'-fluorene) (1) has now been reexamined.

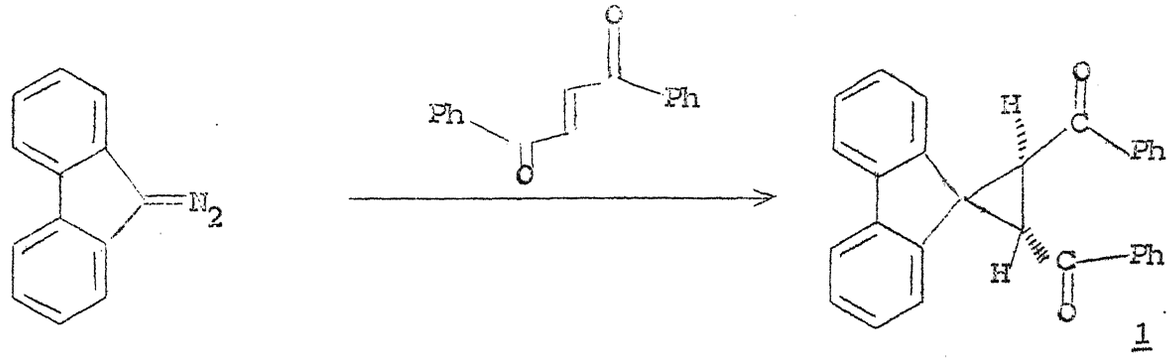
Compound 1 on treatment with methanolic potassium hydroxide followed by hydrogen chloride gives- contrary to earlier report- the rearranged product 2,5-diphenyl-3-(9'-methoxy-9'-fluorenyl)-furan (2), whose structure is established by degradation as well by synthesis involving 2,5-diphenyl-3-(9'-fluorenyl)furan cation generated from 2,5-diphenyl-3-(9'-hydroxy-9'-fluorenyl)furan (6) which in turn was synthesized from 2,5-diphenyl furyl magnesium bromide and fluorenone.

1,2-Dibenzoyl(1-fluorenylidine)ethane (9) has now been identified as the product that was isolated in the previous work from 1 and methanolic potassium hydroxide followed by hydrogen chloride and further the role of 9 as an intermediate in the 1 $\rightarrow$ 2 change has been established. Both 1 and 9 give the same 1,2-dibenzoyl-1-(9'-fluorenyl)ethane (7) whilst 2 undergoes hydrogenolysis to give 2,5-diphenyl-3-(9'-fluorenyl)-furan 8.

Results and Discussion

trans-2,3-Dibenzoylspiro(cyclopropane-1,9'-fluorene)* (1) was prepared in quantitative yields from 9-diazofluorene and

trans-dibenzoyl ethylene:[1]



1

The earlier trans stereochemical assignment is supported from NMR studies of spiro cyclopropanes (Appendix).

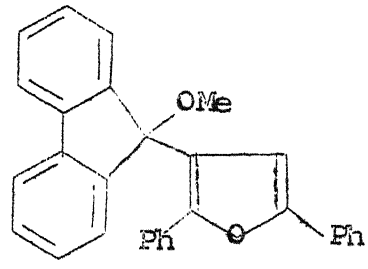
---

* mp 1, 202-203° (lit[1] mp 203°)
IR: ν_{max} (KBr) (cm^{-1}): 1661 (C=O)
NMR: δ ($CDCl_3$): 4.6 (s, cyclopropyl protons), 7.5 (m, aromatic protons.

Reaction of 1 with hot methanolic potassium hydroxide as previously described[1] gave a pink salt from the blood red alkaline solution. The dry salt was unstable and could not be adequately characterized directly. When 1 was reacted with hot methanolic potassium hydroxide followed by treatment with dry hydrogen chloride, as far as possible according to the conditions reported previously,[1**] a pale yellow product mp 112-113° was obtained.

** "Die Blut Rote losung wird filtriert, und es wird solange ein trockner HCl-Gas Strom hindurchgeleitet, bis die Farbe in Gelb umgeschlagen ist. Die heisse losung wird von Kalium Chlorid abfiltriert".

Although the reaction sequence has been repeated many times under these conditions, we have not encountered any compound melting at 195° as reported for this reaction by the earlier workers.[1] Surprisingly the compound obtained, contained a methoxy group, did not show carbonyl absorption and its ultraviolet absorption was quite different from that of 1! This product has been identified as 2,5-diphenyl-3-(9'-methoxy-9'-fluorenyl)furan 2.* The structural assignment is supported by IR, UV, NMR, analysis, degradation and eventually synthesis.[51]



2

---

* IR: ν_{max}(KBr) (cm^{-1}): 1577 (aromatic), 1064 (methoxyl).

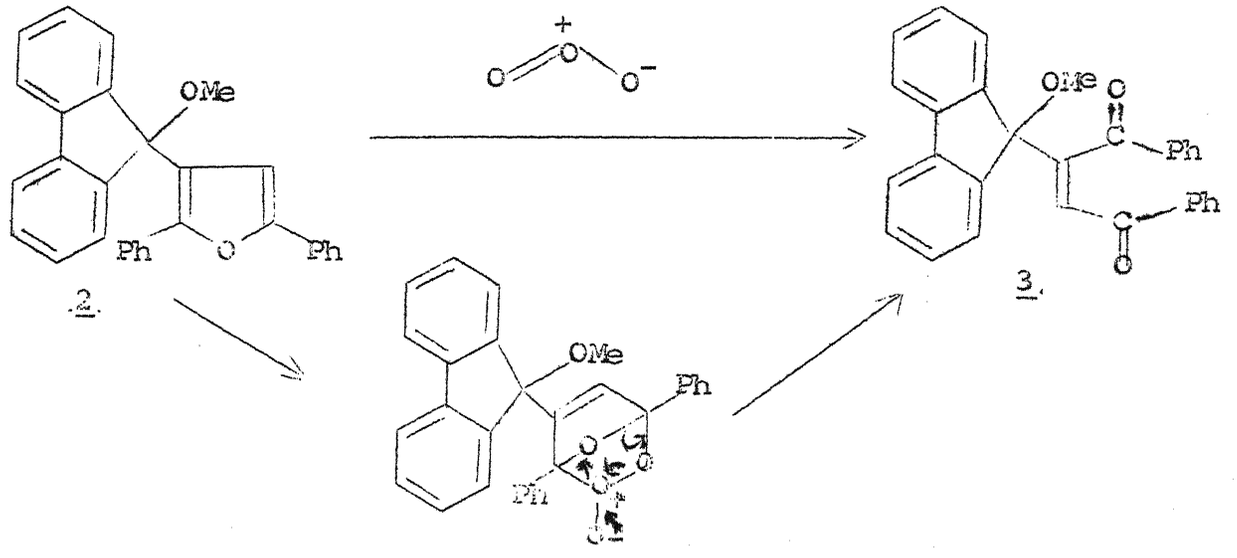
UV: λ_{max}(EtOH): 224 (ϵ,34,150), 229 (ϵ,33,490), 286 (ϵ,25,360), 301 (ϵ,25,250), and 310 (shoulder, ϵ,24,160)nm .

NMR: $\delta_{(CDCl_3)}$: 2.84 (s, $-OCH_3$), 6.9 (s, furan 3H) and 7.4 (m, aromatic 18 protons).

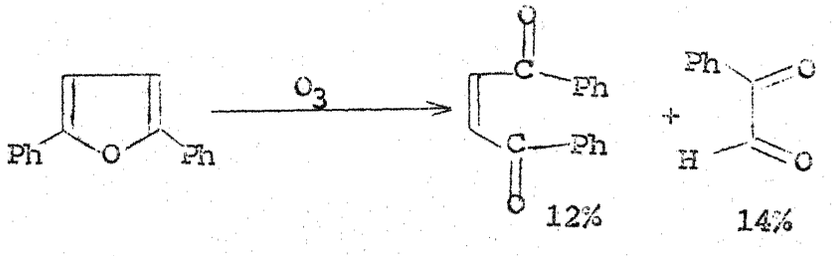
In the light of known transformations of cyclopropyl ketones (IIIB-Background) the 1 → 2 change must be considered novel and at this stage the differences between our results and that reported[1] were perplexing.

Efforts were then made to confirm the structural assignment for 2 by degradation studies.

Ozonolysis of 2 in chloroform gave a white crystalline solid to which structure 3 has been assigned.[51] In this experiment there was also obtained an oil which could not be further characterized. The 2 → 3 change can be rationalized by pathway similar to that involved in the transformation of 2,5-diphenylfuran to cis-1,2-dibenzoylethylene:[52]

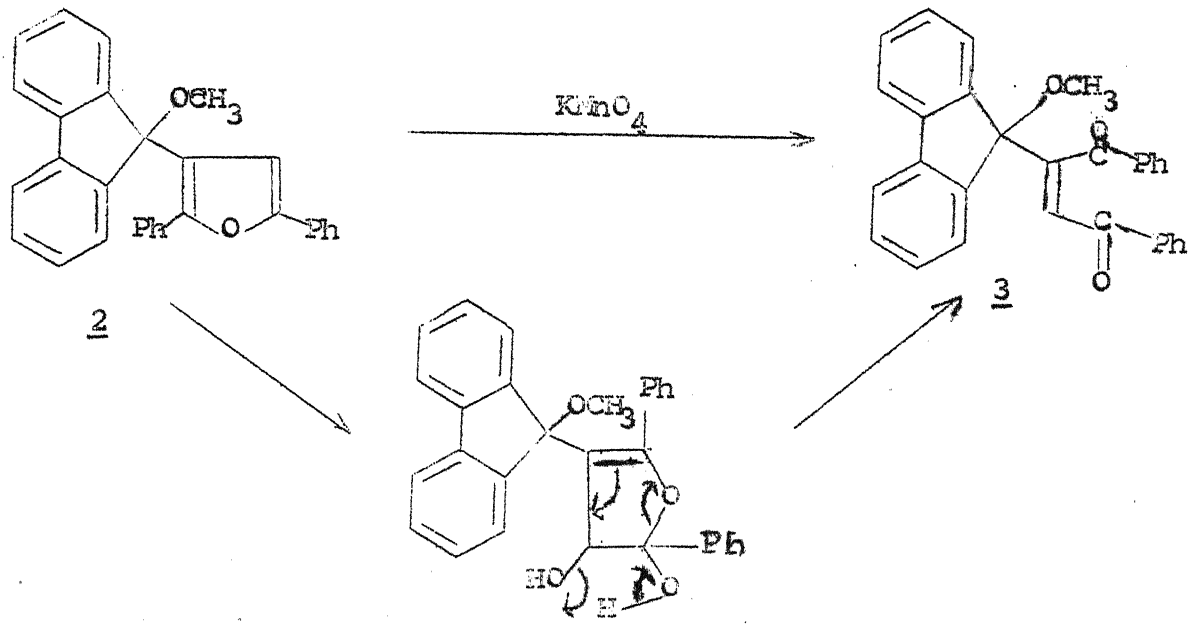


In the reaction of 2,5-diphenylfuran with ozone further ozonolysis of the initially formed cis-dibenzoylethylene takes place to give phenyl glyoxal:[52]



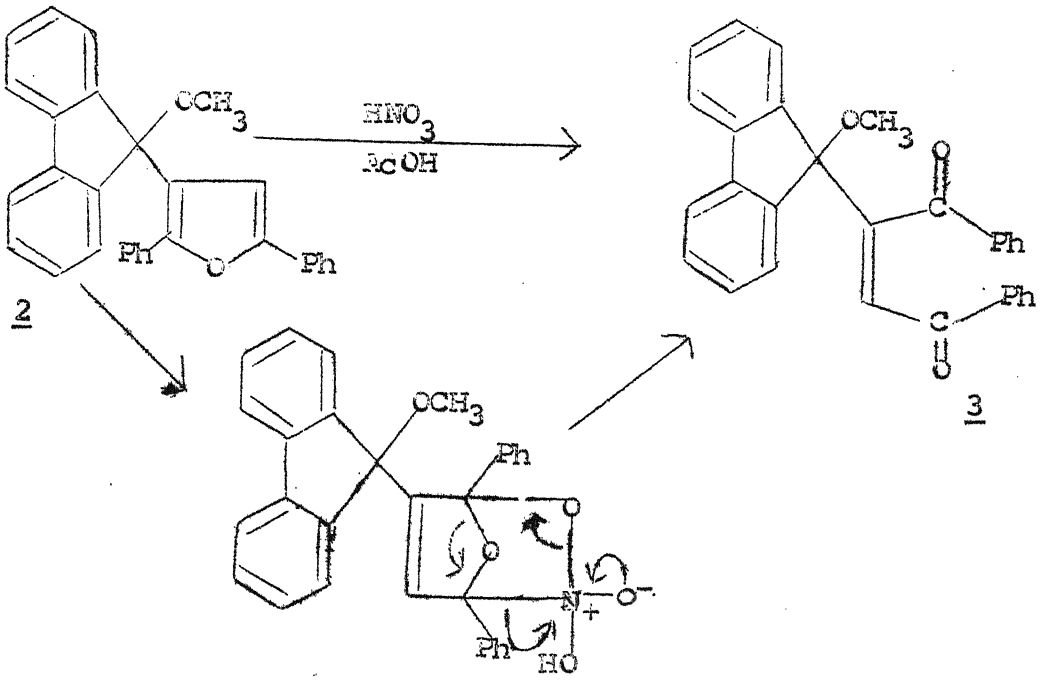
In the present investigation uncharacterized oily products that could be resulting from further degradations were present. In attempts to make the oxidation process more efficient, furan 2 was reacted with buffered potassium permanganate and the same 1,4-diketone 3 was obtained in a much higher yield.

The 2 → 3 change with potassium permanganate has no precedence in furan chemistry and is rationalized as follows:



The most satisfactory method for effecting the 2 → 3 change is the well known nitric acid/acetic acid[53] reagent which infact gave 85% yield of the desired diketone.

This transformation also could be rationalized on the basis of an initial [4 + 2] addition followed by fragmentation in a manner analogous to the transformation of the furan ozonide:



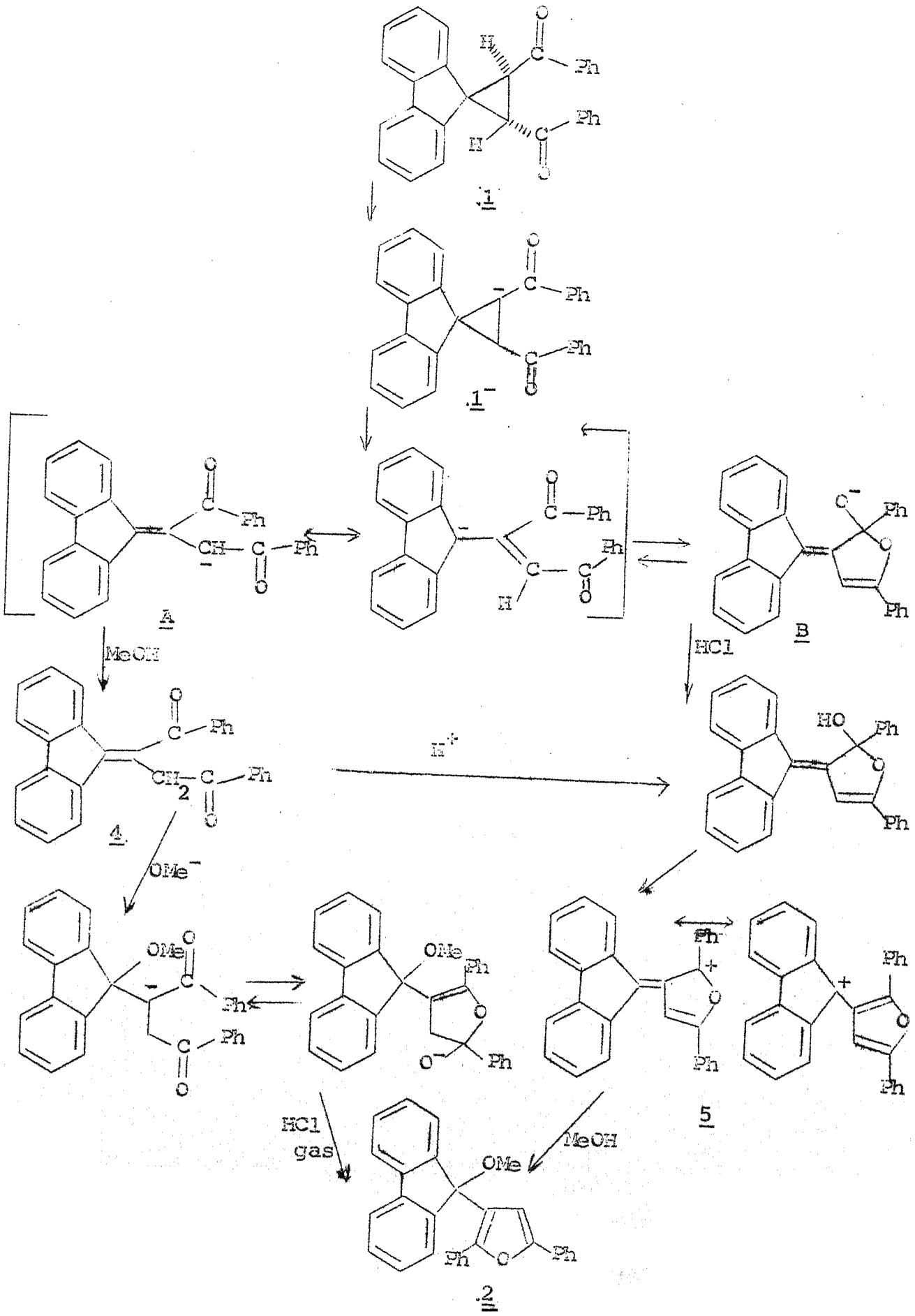
The structural assignment for 3 is supported by analytical and spectral data:*

---

* IR: ν_{max} (KBr) (cm^{-1}): 1681, 1605 (α,β-unsaturated C=O).

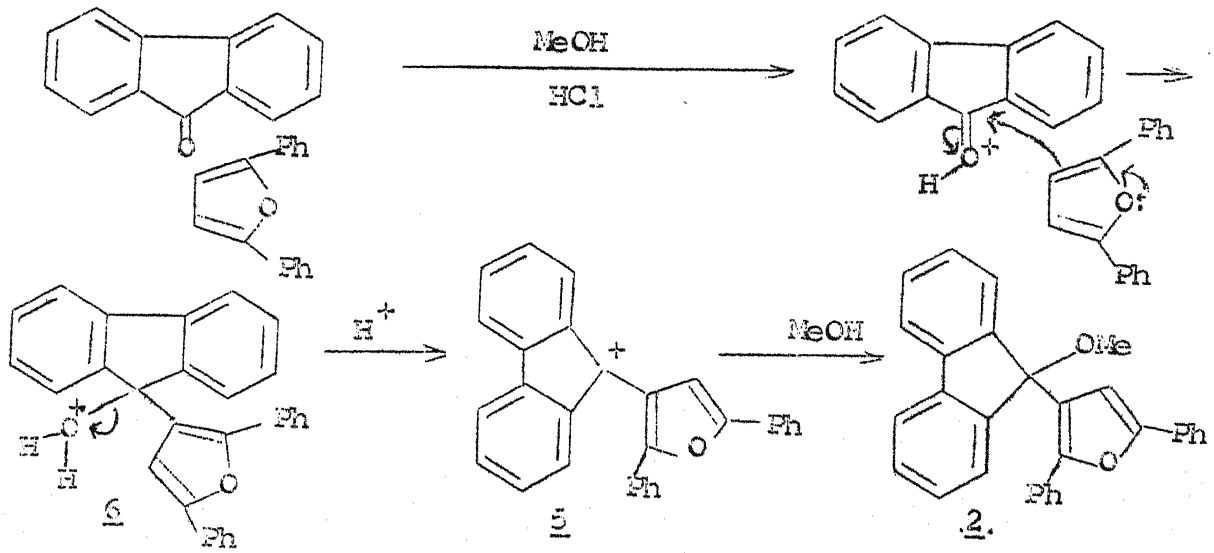
NMR: $\delta_{(CDCl_3)}$: 2.9 (s, $-OCH_3$), and 7.5 (m, aromatic 10 protons and olefinic proton).

Two reasonable mechanisms can be written for the 1 → 2 change, in essence differing only in the sequence involving introduction of the methoxyl function.

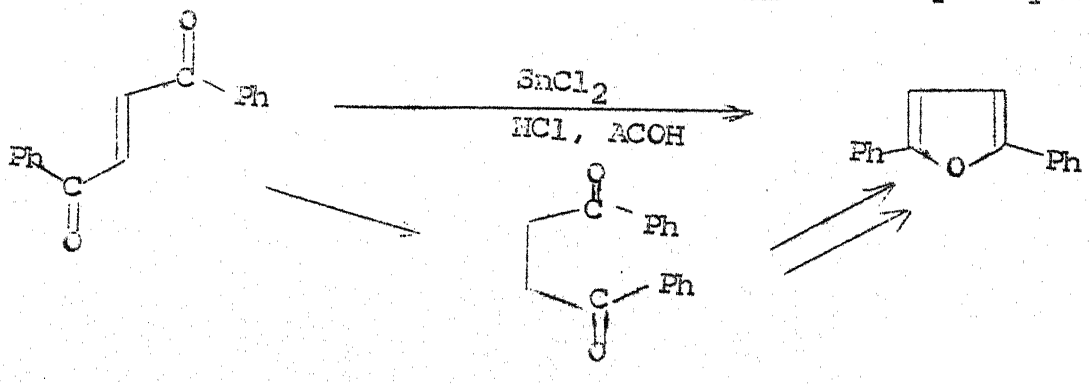

1
1⁻
A
B
MeOH
HCl
4
H⁺
OMe⁻
5
HCl
gas
MeOH
2

The addition of elements of methoxide ion envisaged in path A was considered not very likely because under this highly alkaline condition 4 would be expected to exist largely in the form of its conjugate base as evidenced by the deep red colour of the reaction mixture prior to treatment with hydrogen chloride gas.

The novel cation system represented by 5 was then considered as a likely intermediate and a synthesis of 2 was planned involving this species. Initially ion 5 and subsequently 2 was sought by acid catalysed interaction of 2,5-diphenylfuran and fluorenone:

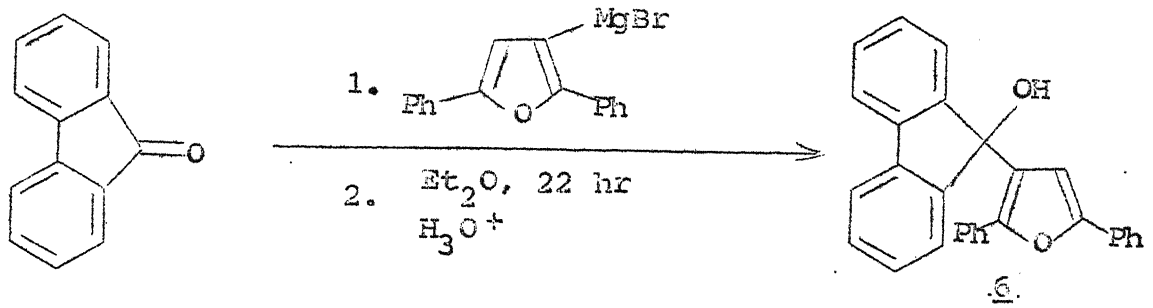


2,5-Diphenylfuran was prepared from trans-dibenzoylethylene:[54]



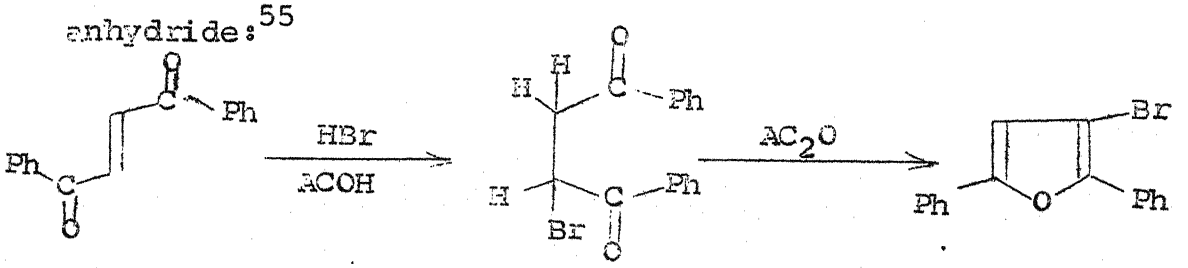
A methanolic solution of equimolar amounts of fluorenone and 2,5-diphenylfuran was saturated with dry hydrogen chloride gas and set aside. No reaction could be detected (TLC!) even on prolonged keeping.

Efforts were then made to prepare 2 involving the alcohol 6 , which was prepared by addition of fluorenone with 2,5-diphenylfuryl magnesium bromide:



6

The precursor of the Grignard reagent, 3-bromo-2,5-diphenylfuran was made by sequence involving hydrobromic acid addition to trans-dibenzoyl ethylene followed by cyclization with acetic anhydride:[55]



The structural assignment for the tertiary alcohol 6 is supported by analytical and spectral data.*

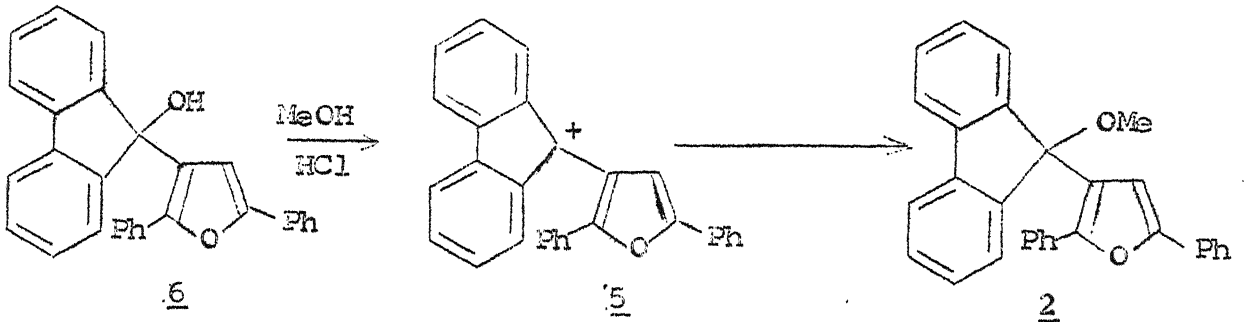
---

* IR: ν_{max} (KBr) (cm^{-1}): 3448 (-OH), 1124 (C-O).

NMR: $\delta_{(CDCl_3)}$: 7.0 (s, 3 furyl proton), and 7.4 (m, aromatic protons).

UV: λ_{max} (EtOH): 215, 231, 238 and 287 nm.

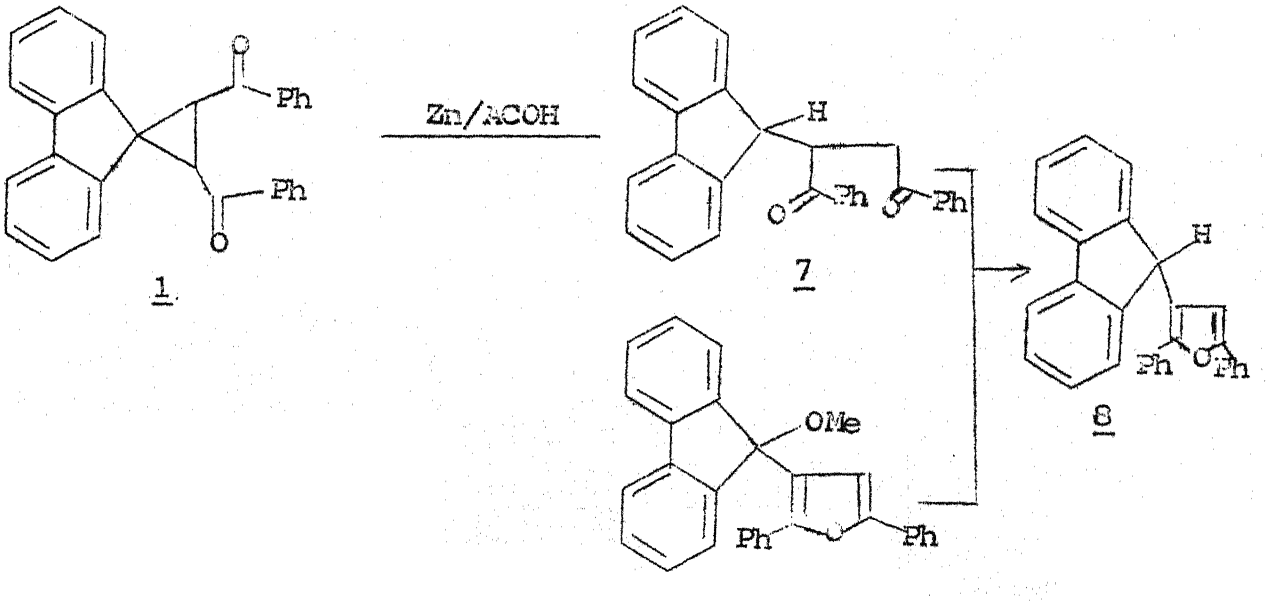
The rationalization of the novel 1 → 2 change involving cation 5 finds much support in the observation that the tertiary alcohol 6 is exceptionally easily transformed to 2 in 88% yield by treatment with methanolic hydrogen chloride!



6 5 2

The identity of 2 obtained from 1 and also 6 was completely established by analysis, mp, IR and NMR.

The possibility that the earlier workers[1] have infact obtained 2, inspite of difference in the melting point, was also considered. Interestingly the observation made by them that both 1 and product arising from treatment with methanolic potassium hydroxide and dry hydrogen chloride gave same compound mp 209° can be accommodated on basis of structure 2!



1 7 8

2

The 1 → 7 change, as reported in the background has ample precedence and the further transformation to 8 is a simple furanization reaction. The compound 2 can be expected to undergo ready hydrogenolysis of the C-OCH_3 bond to give 8.

In the event when 2 was reacted with Zinc-acetic acid-hydrochloric acid under conditions described earlier[1], the compound obtained was indeed the expected furan 8, mp 158-59°. The structural assignment is supported by analytical and spectral results.*

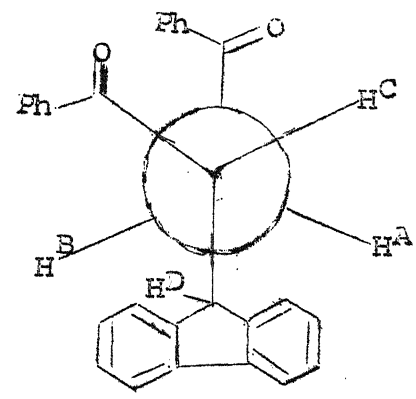
---

* IR: ν_{max} (KBr) (cm^{-1}): did not show the strong C-OCH_3 (1064) absorption present in 2.

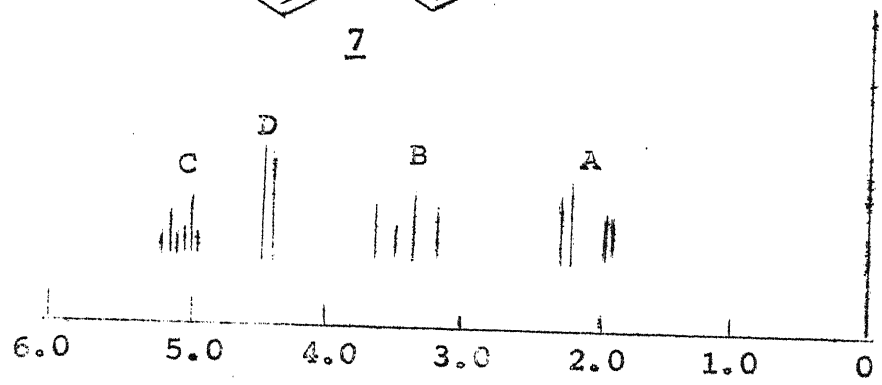
NMR: $\delta_{(CDCl_3)}$: 5.5 (s, 9'-fluorenyl proton), 6.10 (s, furan H), and 7.4 (m, aromatic 18 protons).

On the other hand when 1 was reacted with zinc-acetic acid-hydrochloric acid[1], a compound melting at 212°- for the first time in reasonable agreement with observations earlier reported[1]- was obtained. The furan 8 was totally absent (TLC) in the reaction mixture. This compound has been assigned structure 7 on basis of analytical and spectral data.** (next page).

The most noteworthy feature of 7 is its distinctive ABCD NMR spectrum:



7



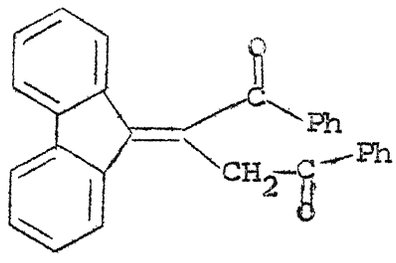
** IR: ν_{max}(KBr) (cm^{-1}): 1664 (-C=O).

NMR: $\delta_{(CDCl_3)}$: 2.1 (d of d, J_{AB}= 18, J_{AC}= 3, A), 3.38 (d of d, J_{AB}= 18, J_{BC}= 10, B), 4.45 (d, J_{CD}= 3, D), and 5.1 (d of t, J_{BC}= 10, J_{AC}= 3, J_{DC}= 3, C), 7.4 (m, aromatic protons).

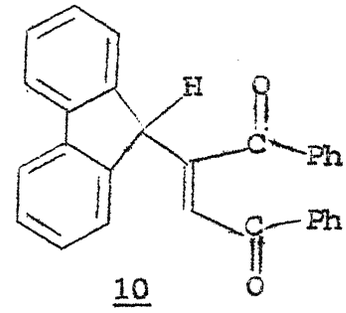
MS: m/e-402.

The reported[1] observations that compound 7 also arise under conditions of the 1 → 7 change from compound mp 195°, resulting from 1 and methanolic potassium hydroxide-hydrogen chloride can be accommodated on the basis of either structure 9 or 10 for the

195° melting compound:



9



10

Of this 9 should be preferred on basis of the reported[1] yellow colour for the 195° melting compound. It might be recalled that in the rationalization of the 1 ⟶ 2 change, compound 9 was considered as a possible intermediate as 4; thus bringing to focus the possibility that both 2 and 9 could arise from common intermediates. Indeed a minor variation of the reported[1] reaction conditions gave the 195° melting substance from 1: The blood red filtrate resulting from 1 and methanolic potassium hydroxide on saturation with dry hydrogen chloride in the cold, precipitated a yellow compound melting at 195°. Interestingly under these conditions no 2 was obtained. Crystallization gave pure material melting at 198° and this compound is now identified as 9 on basis of analytical and spectral data.*

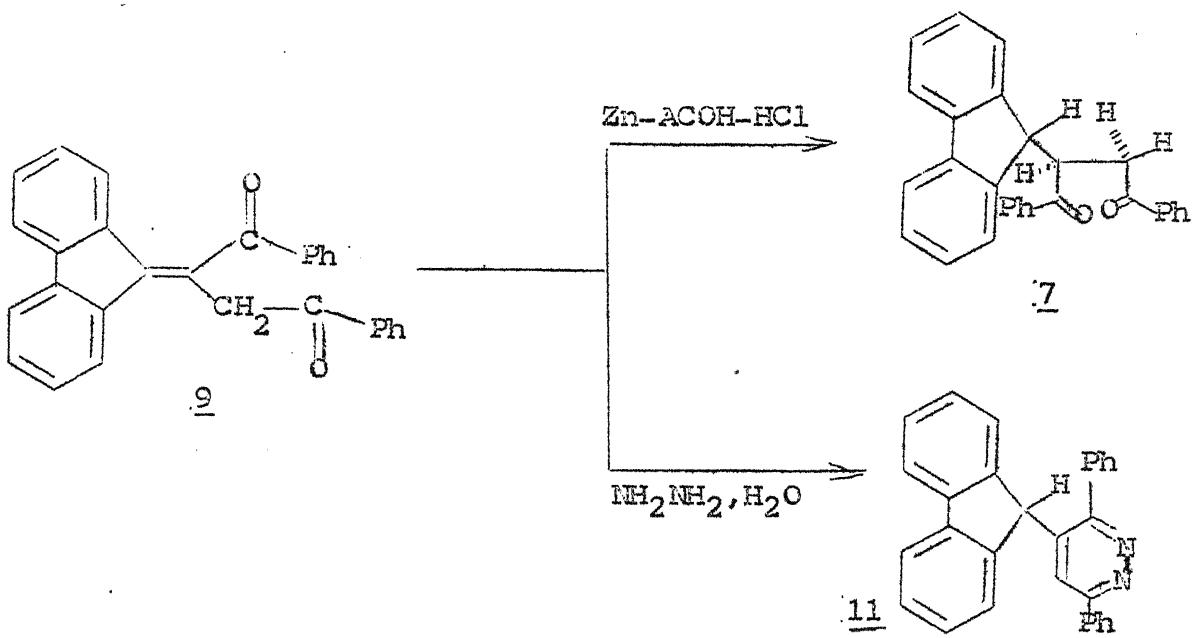
---

* IR: ν_{max}(KBr) (cm^{-1}): 1692, 1661 (C=O).

NMR: $\delta_{(CDCl_3)}$: 4.81 (s, methylene protons) and 7.4 (m, aromatic protons

---

Compound 9 gave on reduction with zinc-acetic acid-hydrochloric acid the compound 7 and on treatment with hydrazine hydrate gave the aromatic system 11.



9 7 11

The structural assignment for the novel aromatic system 11 is supported by analytical and spectral data.*

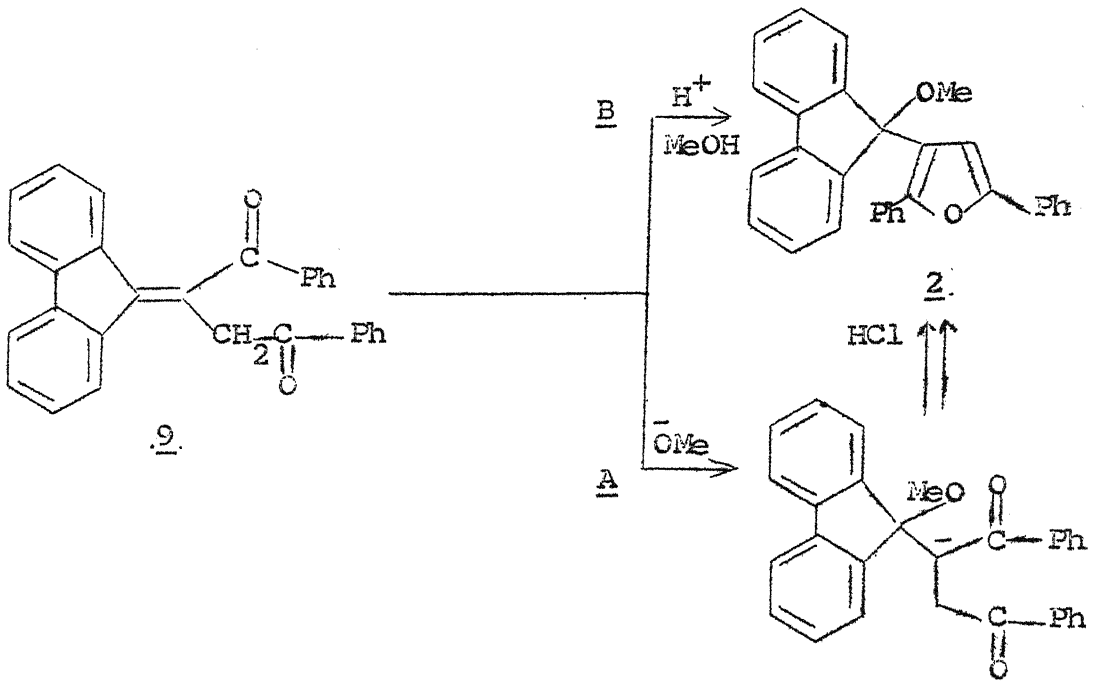
---

* NMR: $\delta_{(CDCl_3)}$: 5.45 (s, 9'-fluorenyl H) and 7.4 (m, aromatic protons).

The melting points of 7 and 11 are close to that reported[1] for similar transformations of the 195° melting compound and consequently it is almost certain that the 195° melting compound obtained earlier has structure 9.

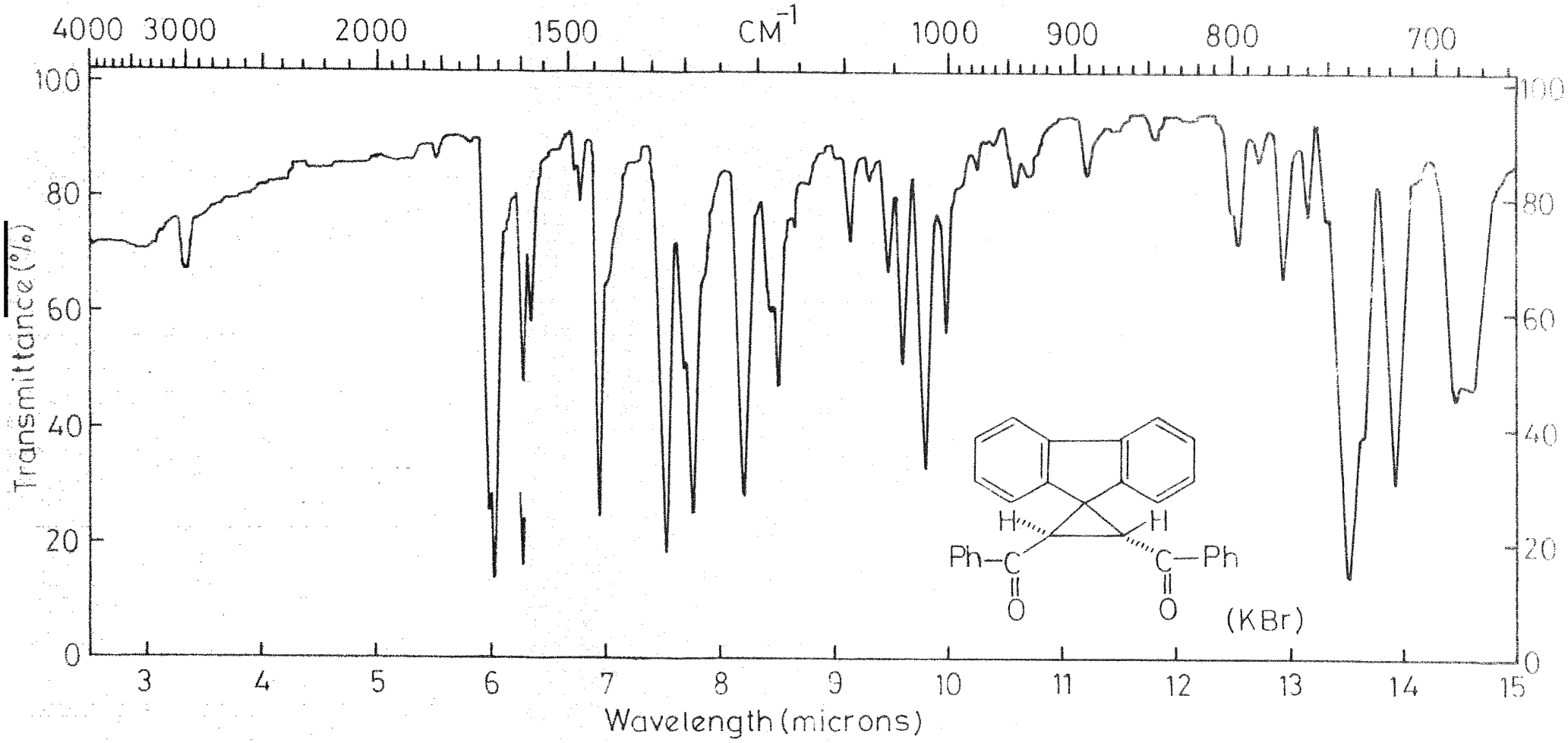
As discussed earlier 2 could arise from 9 by two

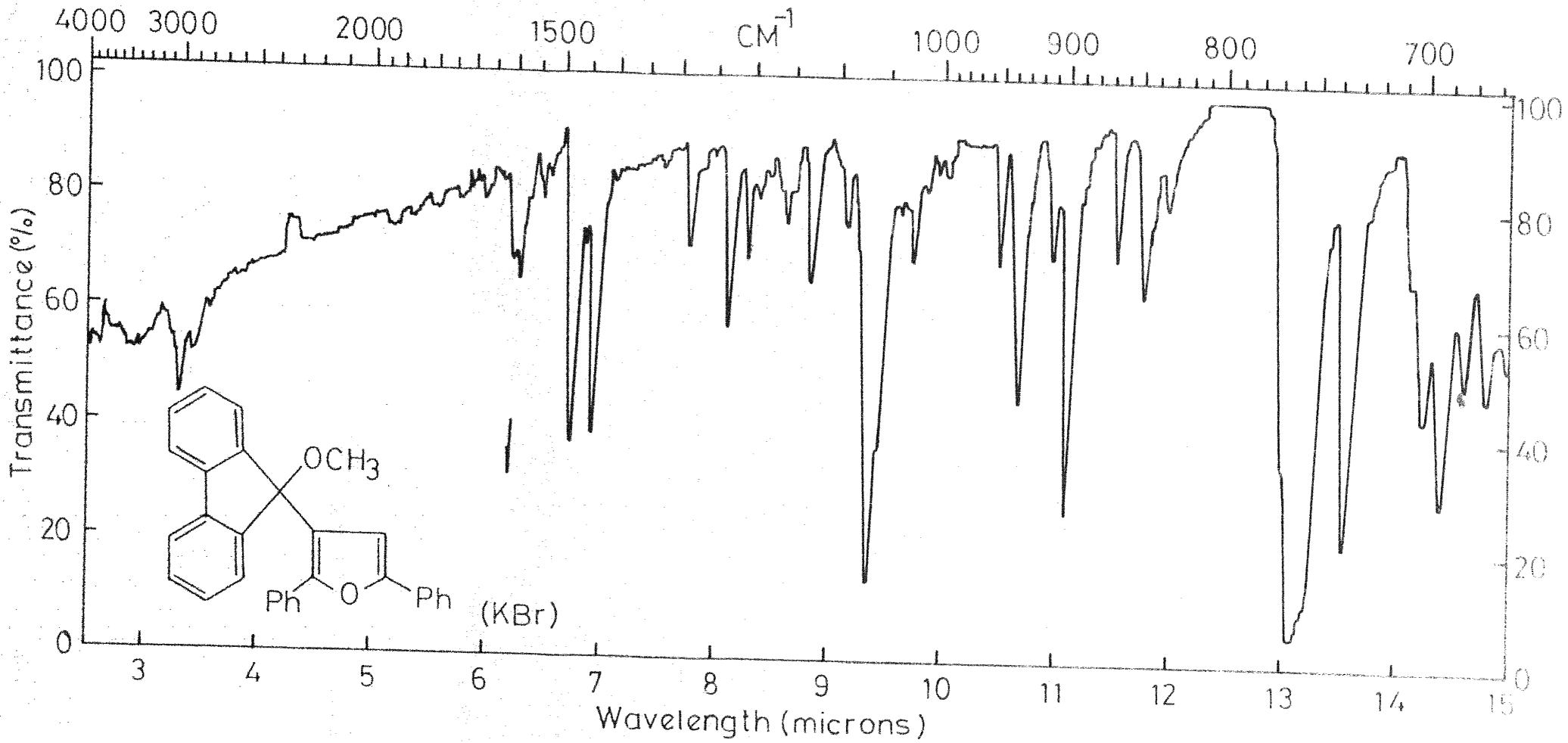
pathways:

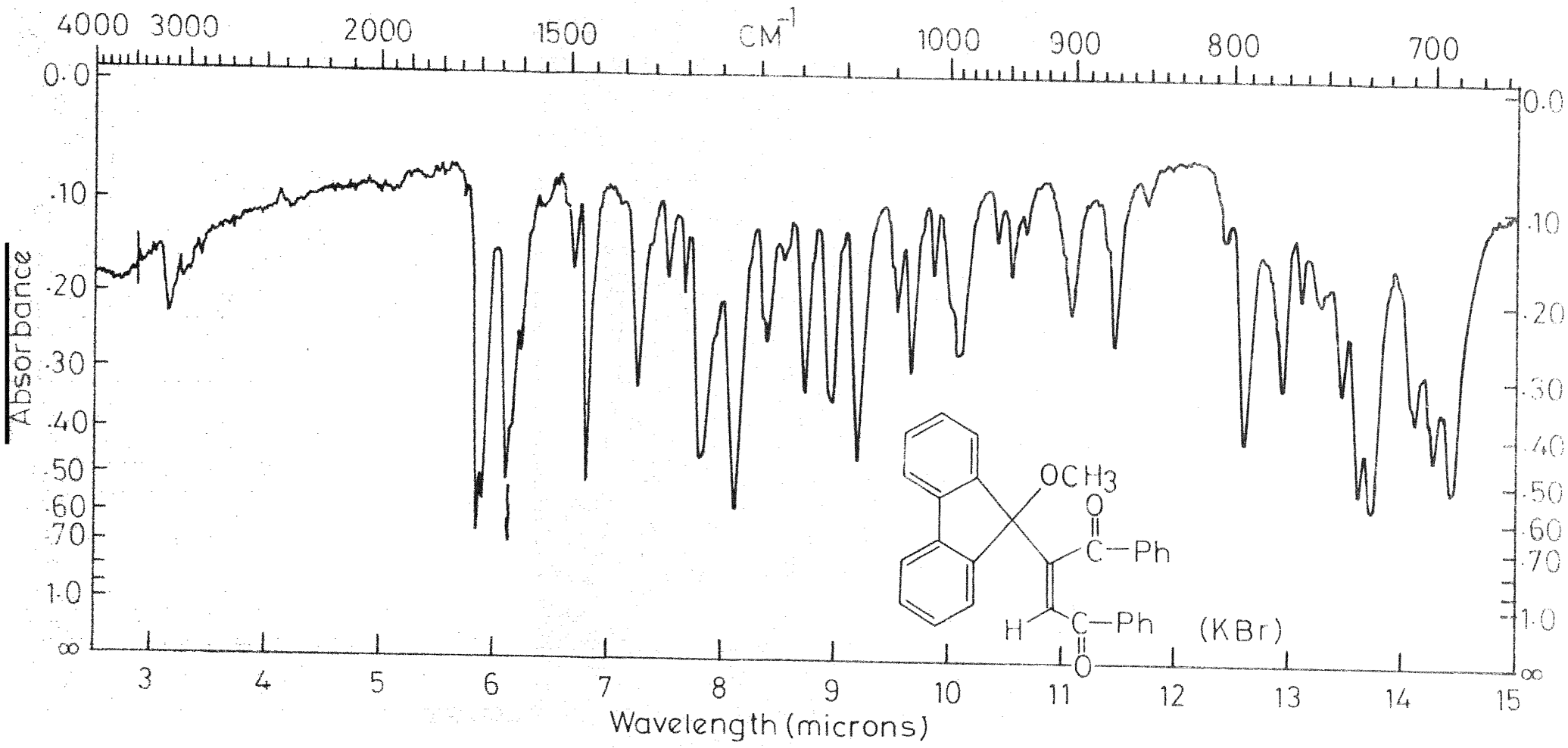


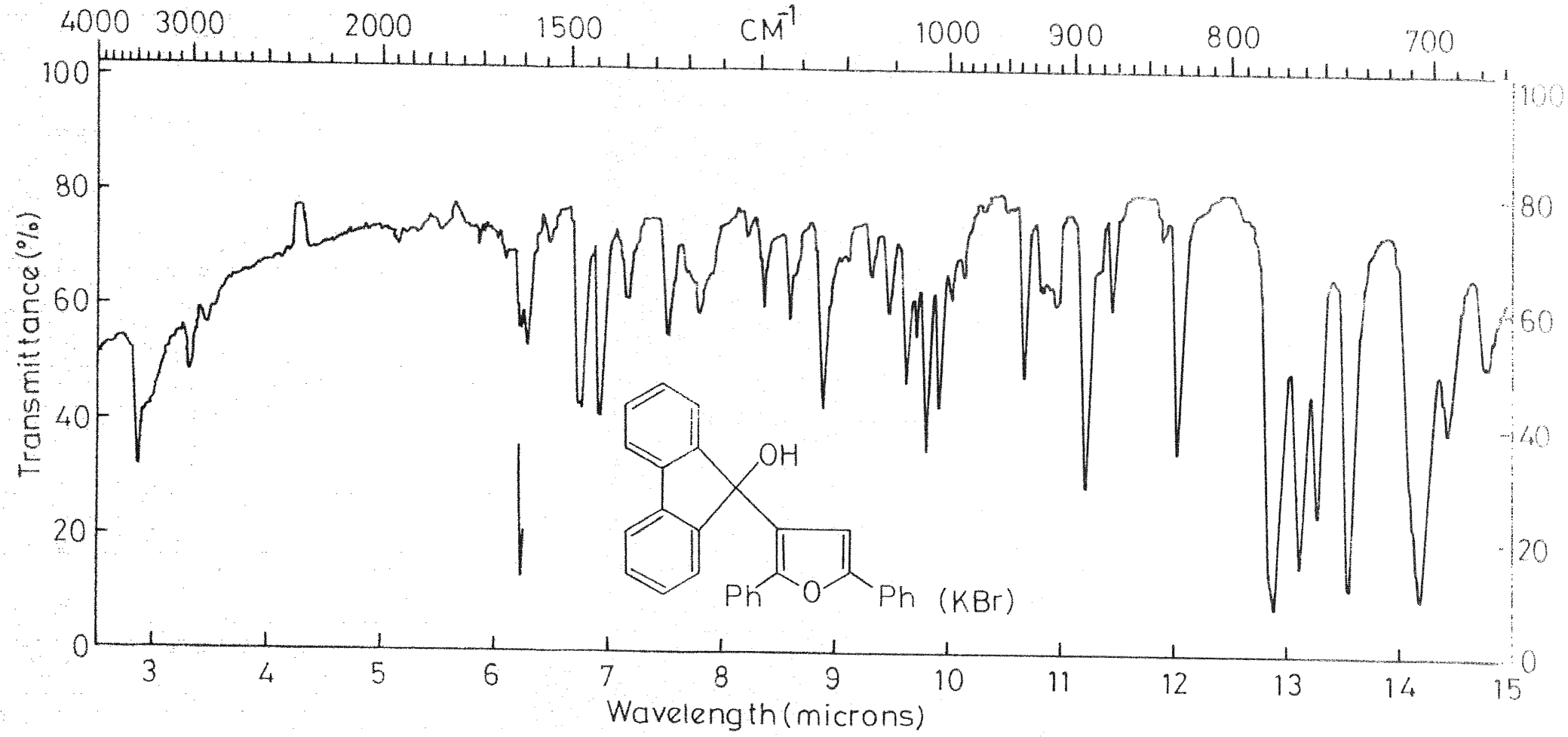
The colour of the alkaline solution resulting from 1 makes pathway A unlikely and accordingly reaction of 9 with methoxide followed by dry hydrogen chloride gave a complex mixture in which 2 was present only to a small extent. In contrast, reaction of 9 with hot methanolic hydrogen chloride gave cleanly 2 and consequently the rationalization of the 1 → 2 change involving 9 receives strong support. Interestingly both 9 and 2, whilst sparingly soluble in cold methanol are quite soluble in hot solvent. On basis of this the apparently startling change in the course of the reactions of 1 as a function of temperature can be readily explained. When the hydrogen chloride saturation is conducted in the cold, the initially formed 9 precipitates and no further reaction takes place.

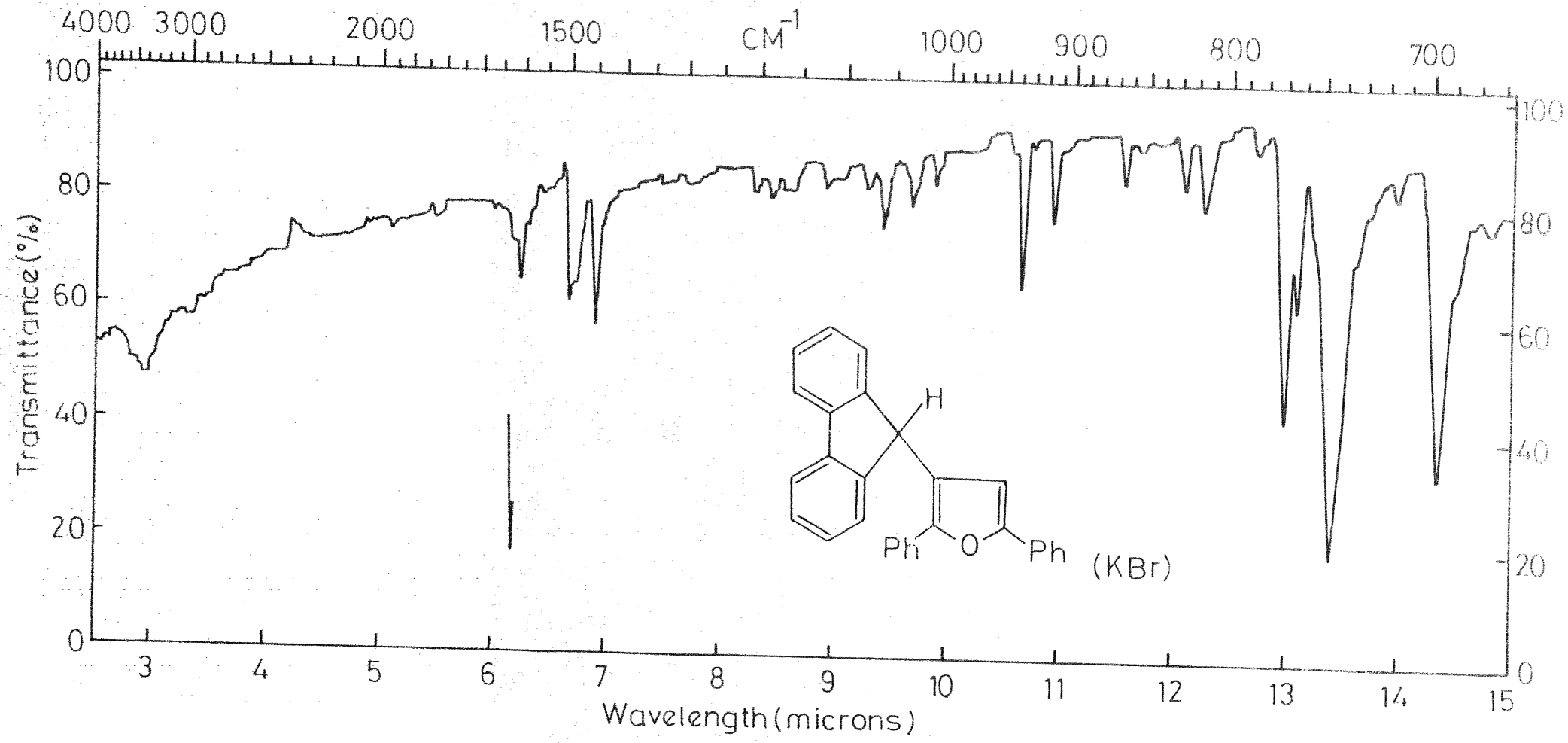
In contrast *in the hot*, the resulting **9** is soluble and is rapidly transformed to the furan **2**. It should be mentioned that the possibility of **2** arising independently of **9** could not be totally excluded.

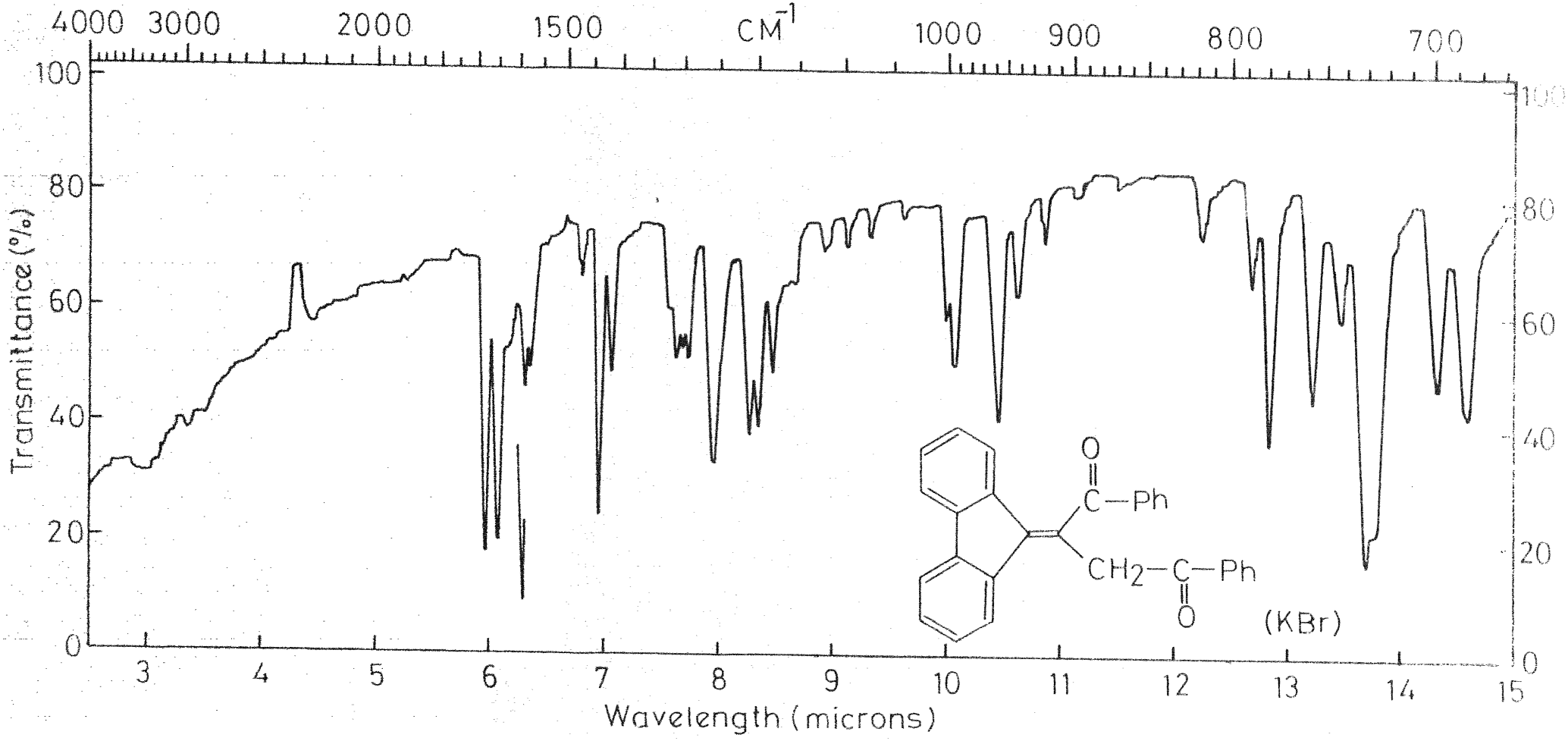

4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
100
80
60
40
20
0
Transmittance (%)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)
H
H
Ph—C
C—Ph
O
O
(KBr)


4000 3000 2000 1500 CM^{-1} 1000 900 800 700
100
80
60
40
20
0
Transmittance (%)
OCH$_3$
Ph
O
Ph
(KBr)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)


4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
0·0 ·10 ·20 ·30 ·40 ·50 ·60 ·70 1·0 ∞
Absorbance
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)
OCH3
O
C—Ph
H
C—Ph
O
(KBr)


4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
100
80
60
40
20
0
Transmittance (%)
OH
Ph O Ph
(KBr)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)


4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
100
80
60
40
20
0
Transmittance (%)
H
Ph
O
Ph
(KBr)
3 4 5 6 7 8 9 10 11 12 13 14 15
Wavelength (microns)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Wavelength (microns)
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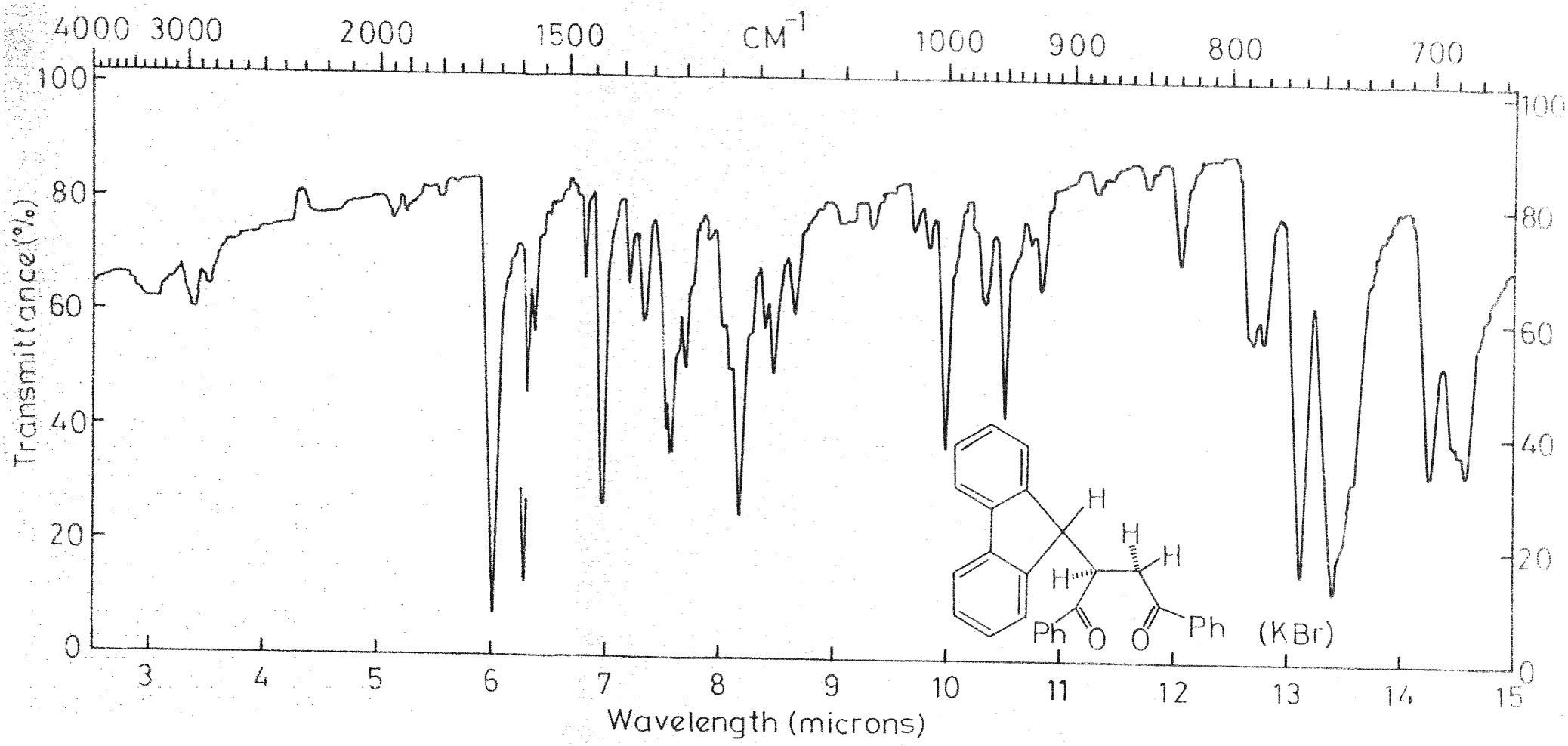
C—Ph
CH2—C—Ph
O
(KBr)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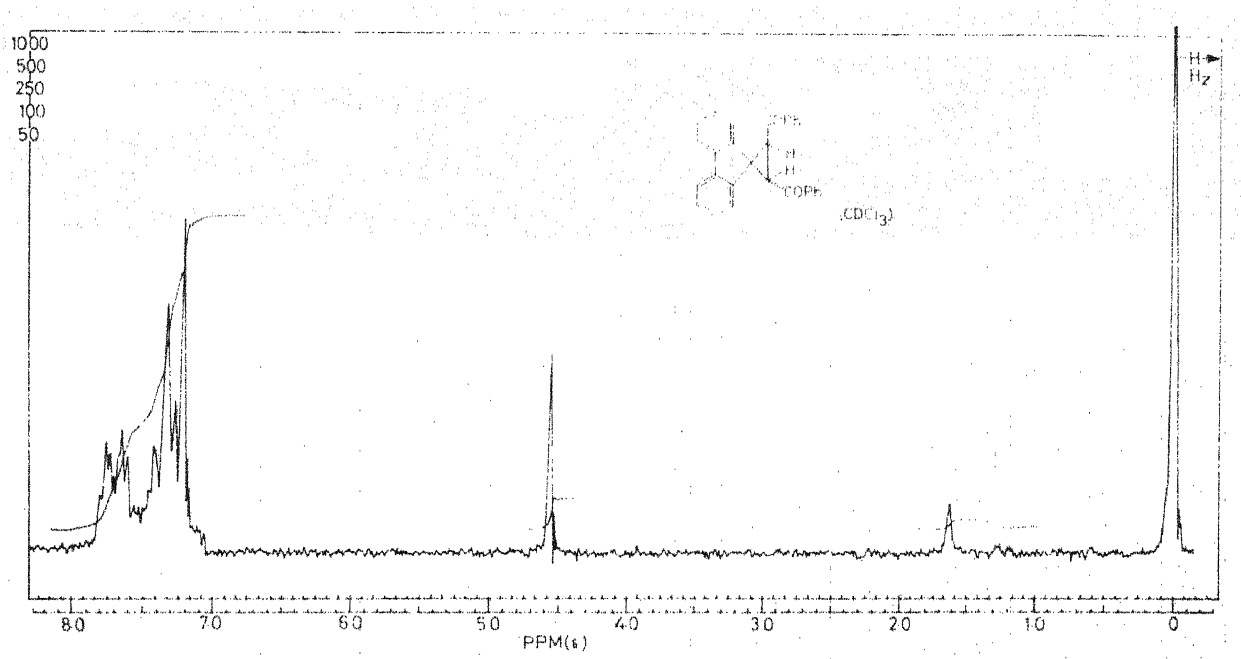
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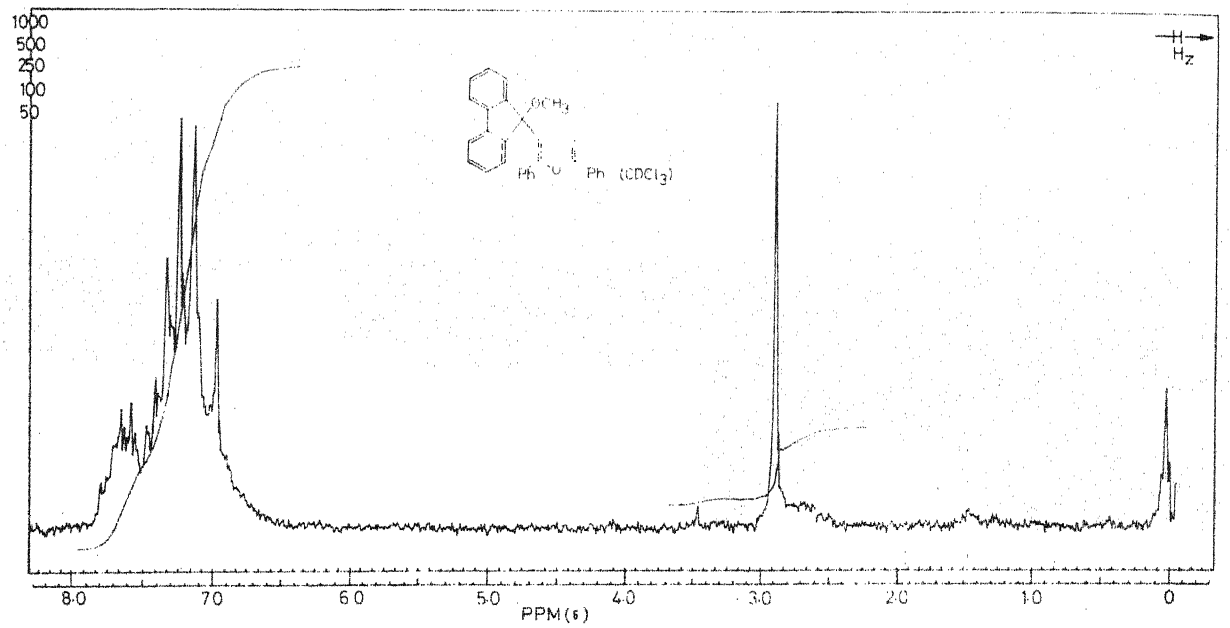
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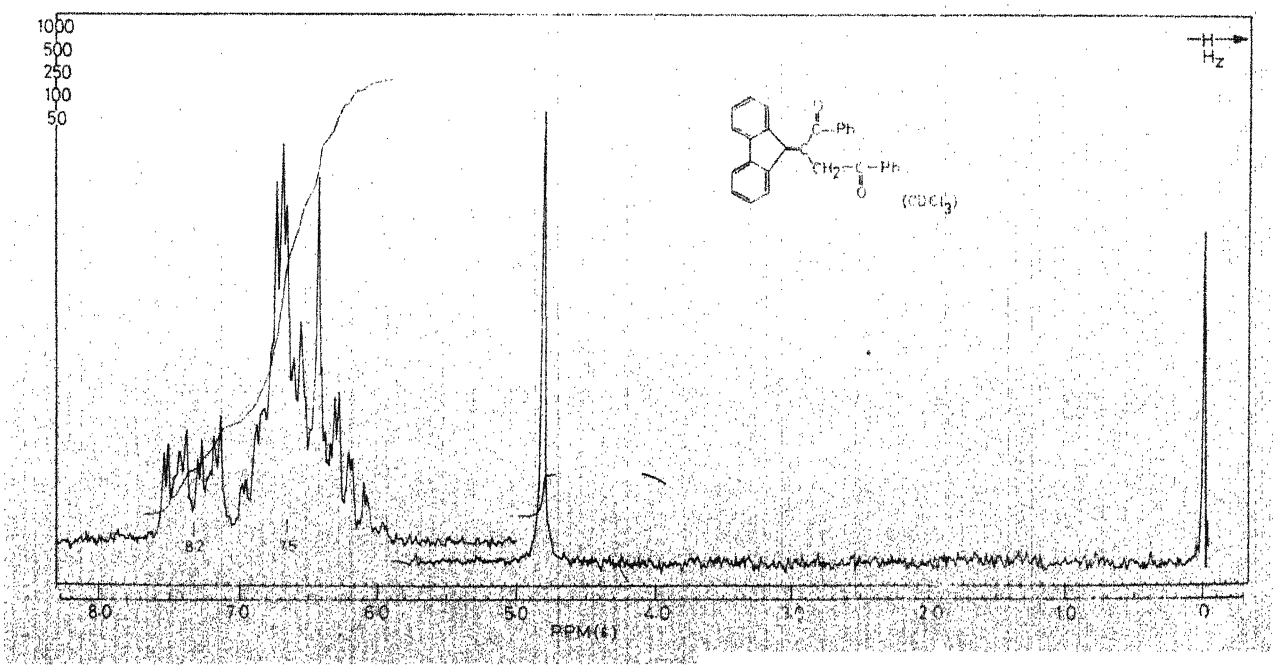
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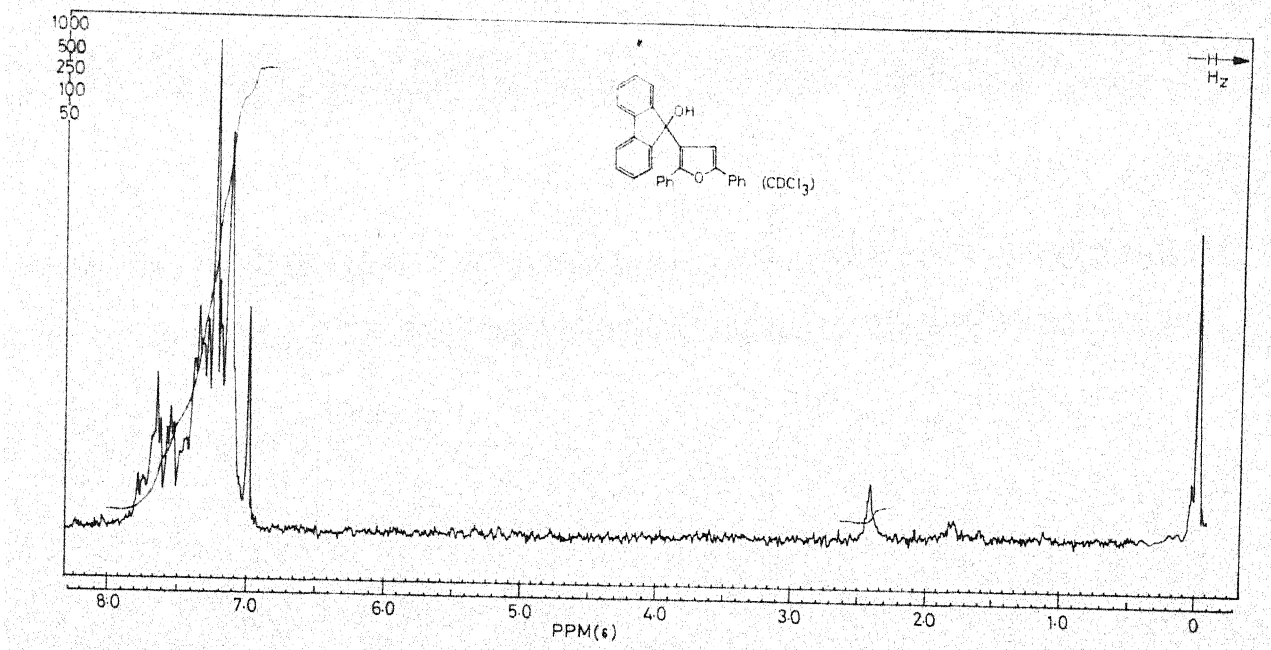
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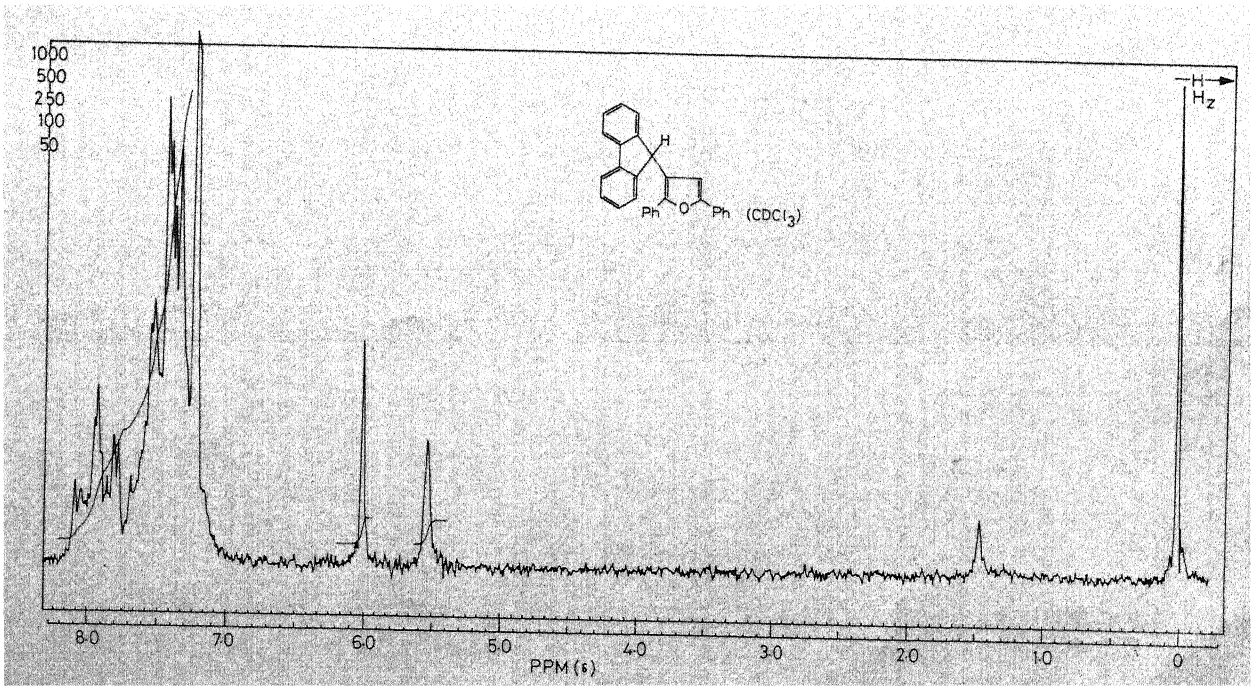
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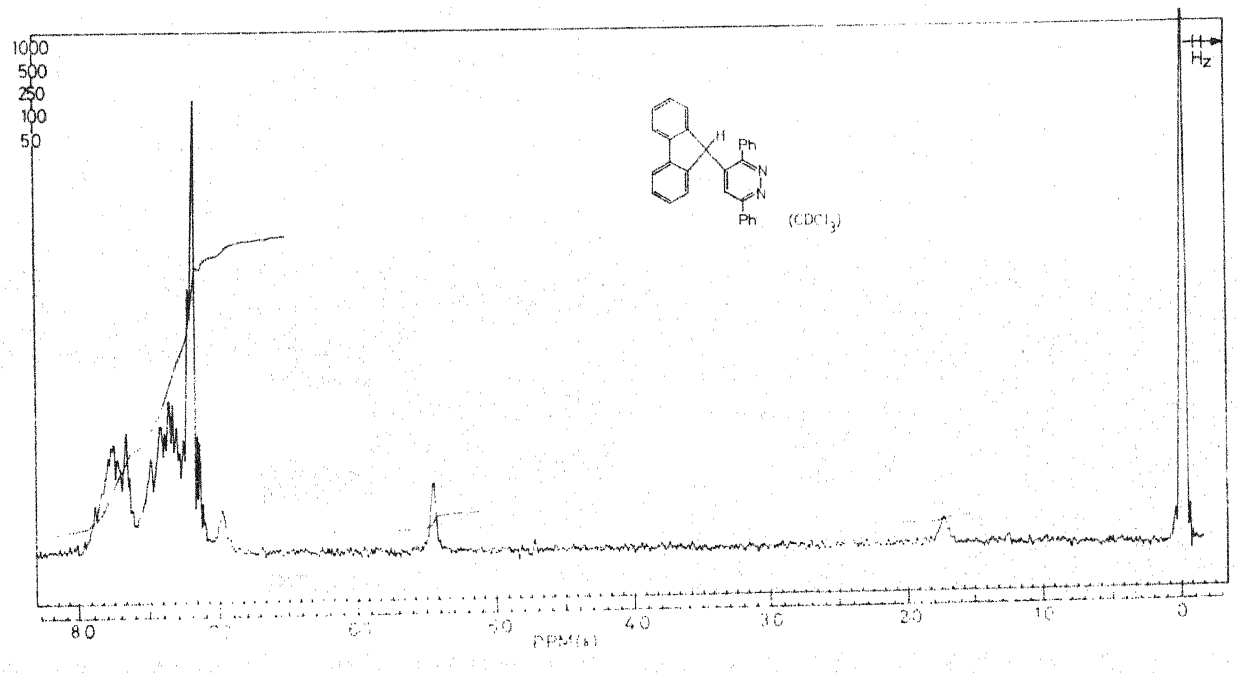
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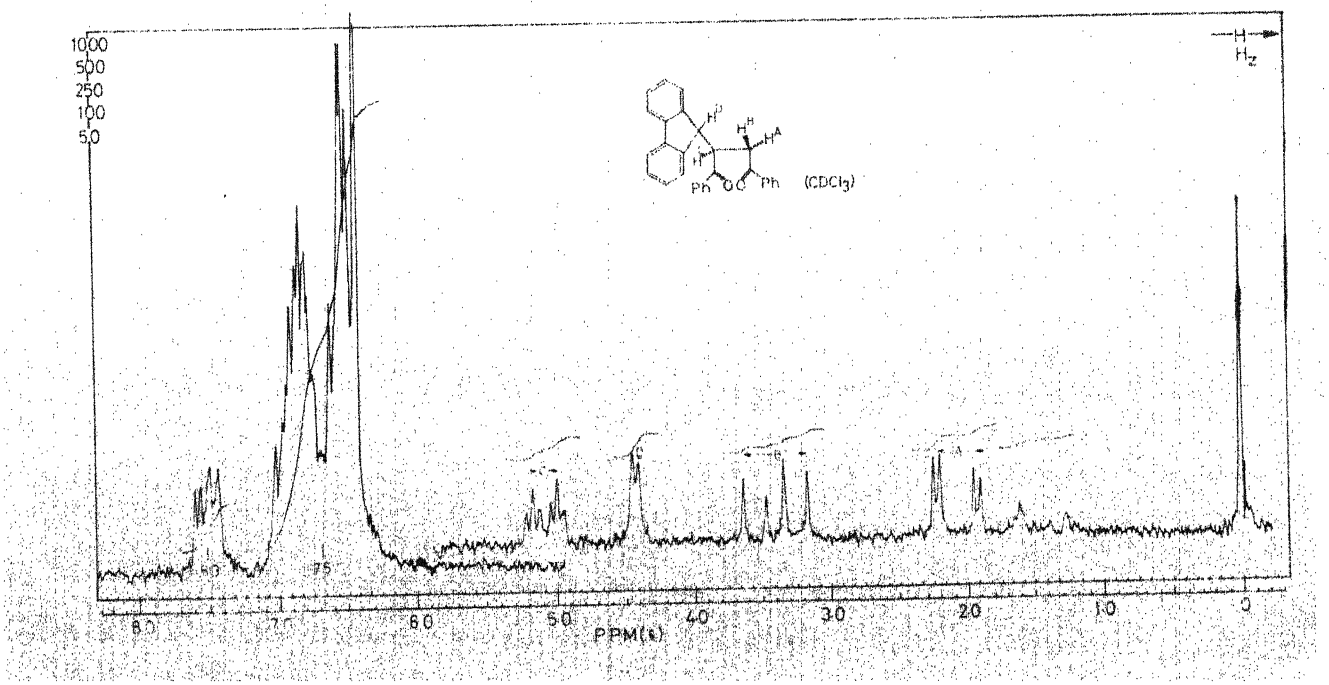
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(CDCl3)
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PPM(δ)

III.E EXPERIMENTAL

GENERAL

Melting points are uncorrected and were determined on a Thomas Hoover capillary melting point apparatus. Infrared spectra were determined on Perkin-Elmer model 137 recording spectrophotometer. NMR spectra were recorded on Varian A-60D instrument using tetramethylsilane (TMS) as internal standard. Ultraviolet spectra were recorded on Cary-14 instrument. Silica gel G (Stahl) was used for thin layer chromatography and column chromatography was done on silica gel (BDH), columns being prepared from its slurry in petroleum ether (60-80°).

Fluorenone

In a 1 l. three-necked flask fitted with a mechanical stirrer, a dropping funnel and a water condenser, was placed technical fluorene (50 g, 0.30 mol). Glacial acetic acid (100 ml) was added and the mixture was heated to gentle boiling. Sodium dichromate dihydrate (157 g, 0.06 mol) was dissolved in a warm mixture of 200 ml of glacial acetic acid and 50 ml of water. This solution was added dropwise to the boiling solution of fluorene over a period of 0.5 hr. After stirring for additional 3 hr at refluxing temperature, the mixture was poured into 1 l. of ice-cold water. After standing for 2 hr, an yellow solid precipitated out. The solid was filtered, washed with water and distilled at 110-115° at 1 mm. The distillate was dissolved in the minimum amount of benzene and petroleum ether

(bp 40-60°) was carefully added. On standing 32 g (60%) of yellow crystals were obtained, mp 82-83° (lit[56] mp 83-83.5°)

Fluorenone Hydrazone

Fluorenone (18.0 g, 0.10 mol) was dissolved in the minimum amount of 95% alcohol and hydrazine hydrate (85%, 8.0 g, 0.13 mol) was added and the mixture refluxed for 6 hr. Yellow crystals of fluorenone hydrazone (18.0 g, 94% yield) was obtained on cooling, mp 148-50° (lit[57] 148-50°).

9-Diazofluorene

A suspension of finely ground mixture of fluorenone hydrazone (4.0 g, 0.02 mol), yellow mercuric oxide (7.0 g) and anhydrous sodium sulphate (2.0 g) in dry ether (50 ml) was stirred for 0.5 hr after addition of 0.5 ml of saturated ethanolic potassium hydroxide. The reaction mixture was filtered and solvents evaporated without heating to give 3.4 g (85%) of 9-diazofluorene, mp 98° (lit[58] 98-99°).

trans-2,3-Dibenzoylspiro(cyclopropane-1,9'-fluorene)

Benzene (50 ml) was poured into a mixture of trans-dibenzoylethylene (8.0 g, 0.034 mol) and 9-diazofluorene (6.4 g, 0.034 mol). The clear red solution warmed up after an induction period and gave off nitrogen rapidly. In 10 min the theoretical amount of nitrogen was collected. During this time the crude dibenzoyl adduct precipitated; yield 13.54 g, crystallization from refluxing benzene gave 11.0 g (66%) of snow white crystals,

mp 202-203° (lit[1] mp 203°).

Anal. Calcd for $C_{29}H_{20}O_2$ (M.wt. 400): C, 87.0; H, 5.0. Found: C, 86.87; H, 4.92.

IR: ν_{max}(KBr) (cm^{-1}): 1661 (C=O).

NMR: $\delta_{(CDCl_3)}$: 4.6 (s, cyclopropyl protons), and 7.5 (m, aromatic protons).

TLC: Single spot (R_f: 0.58, benzene).

Preparation of "Dipotassium salt" of the Dibenzoyl adduct

The dibenzoyl adduct 1 (2.0 g, 0.005 mol) was suspended in 50 ml of 20% methanolic potassium hydroxide and the mixture refluxed for 0.75 hr. The clear blood red solution deposited deep violet needles when allowed to stand at room temperature for 2 hr. The material was collected and washed with 1% methanolic potassium hydroxide solution and dried. Attempts to purify the crude product were not successful.

Reaction of trans-2,3-Dibenzoylspiro(cyclopropane-1,9'-fluorene) (1) with Methanolic Potassium Hydroxide; Isolation of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (2)

To a suspension of 1 (5.0 g, 0.0125 mol) in absolute methanol (125 ml) was added 30% methanolic potassium hydroxide (25 ml) and the red mixture was refluxed for 0.5 hr. The hot solution was filtered and the hot filtrate was treated with dry hydrogen chloride until it became yellow. The mixture was filtered and the filtrate cooled. The yellow precipitate was collected,

washed free of acid and dried to give crude 2 (2.754 g) mp 113-20°. Crystallization from methanol gave pure 2 (2.283 g, 44.3%), mp 122-23°.

Anal. Calcd for $C_{30}H_{22}O_2$ (M.wt. 414): C, 86.95; H, 5.31; $-OCH_3$, 7.49. Found: C, 86.80; H, 5.19; $-OCH_3$, 7.80.

IR: ν_{max}(KBr) (cm^{-1}): 1577 (aromatic) and 1064 (methoxyl).

UV: λ_{max}(EtOH): 224 (ϵ,34,150), 229 (ϵ,33,490), 286 (ϵ,25,360), 301 (ϵ,25,250), and 310 (shoulder; ϵ,24,160) nm.

NMR: $\delta_{(CDCl_3)}$: 2.84 (s, $-OCH_3$), 6.9 (s, furan 3H) and 7.4 (m, aromatic 18 protons).

TLC: Single spot (R_f: 0.71 (benzene)).

The methanolic filtrate after removal of the yellow solid was evaporated to dryness under reduced pressure and a yellow residue (~0.84 g) melting over a range was obtained. An attempt was made to purify this material by chromatography over neutral alumina but the material decomposed on the column.

Attempted Preparation of the Inner Azine from 2

To a warm solution of 2 (0.10 g, 0.00025 mol) in ethanol (3 ml) was added hydrazine hydrate (0.2 ml) and the mixture refluxed for 6 hr (no change in colour!), cooled, filtered and the residue washed with small amounts of ethanol and dried to give 0.082 g, mp 120-23° of the starting material.

Oxidation of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (2) with Nitric Acid; Isolation of 1,2-Dibenzoyl-1-(9'-methoxy-9'-fluorenyl)ethylene (3)

To a stirred suspension of the furan 2 (0.09 g, 0.00022 mol) in glacial acetic acid (0.5 ml) was added a mixture of nitric acid (con, d ~1.42, 0.1 ml) in glacial acetic acid (0.3 ml). The mixture became clear in 0.25 hr. After 0.5 hr, a white solid precipitated from the solution. Stirring was continued for another 0.5 hr. After excess ice-water had been added, the precipitate was collected, washed free of acid, dried and crystallized from ethanol to give pale yellow crystals of 3 (0.079 g, 85%), mp 159-60°.

Anal. Calcd for $C_{30}H_{22}O_3$ (M.wt. 430): C, 83.72; H, 5.1. Found: C, 83.71; H, 4.97.

IR: ν_{max}(KBr) (cm^{-1}): 1681, 1605 (α,β-unsaturated C=O).

NMR: $\delta_{(CDCl_3)}$: 2.9 (s, $-OCH_3$), 7.5 (m, aromatic 18 protons and olefinic proton).

TLC: Single spot (R_f: 0.62 (benzene:ethylacetate (50:50)).

Oxidation of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (2) with Potassium Permanganate

A solution of the furan 2 (0.2 g, 0.0005 mol) and potassium permanganate (0.40 g, 0.0025 mol) in acetone-water-acetic acid (26-3-0.5 ml) was stirred at room temperature for 2 hr. Sodium bisulphite was added and the mixture was made strongly acidic with dilute hydrochloric acid. After most of the acetone had

been removed under reduced pressure, the residue was extracted with excess ether, washed with saturated sodium bicarbonate, dried ($MgSO_4$) and evaporated. The residual oil (~0.2 g) on trituration with ether gave 3 (0.10 g, 40%), mp 160-61°.

Ozonolysis of 2

A solution of the furan 2 (0.40 g, ~0.001 mol) in methylene chloride was ozonized at ~-40° for 20 min. The ozonide was reduced with zinc dust and a trace of hydroquinone. The crude product on trituration with ether gave 3 (0.064 g, 15.2%), mp 159-61°.

Attempted Synthesis of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)-furan (2) from 2,5-Diphenylfuran and Fluorenone:

2,5-Diphenylfuran

trans-Dibenzoylethylene (5.5 g, 0.025 mol) was added portionwise to a vigorously stirred and refluxing solution of 5.5 g of stannous chloride and 11 g each of conc hydrochloric acid and glacial acetic acid. After additional 0.25 hr reflux the reaction mixture was allowed to cool to 50° and poured onto cold water. The solidified portion was crystallized slowly from ethanol to give 2.23 g (37%) of 2,5-diphenylfuran, mp 82-84° (lit[54] mp 86-90°).

Reaction of 2,5-Diphenylfuran with Fluorenone in Methanolic Hydrogen Chloride

Dry hydrogen chloride gas was passed through a solution of 2,5-Diphenylfuran (1 g, 0.005 mol) and fluorenone (0.9 g, 0.005 mol)

in absolute methanol (20 ml) for 0.5 hr. There was no precipitate. TLC showed no reaction.

Synthesis of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (2):

(i) sym-Dibenzoylbromoethane

trans-Dibenzoylethylene (10 g, 0.042 mol) was stirred with 5 g of fuming hydrogen bromide in 30 ml of acetic acid for 4 hr. The suspension was filtered and dried to give 11.6 g (87%) product melting at 181-182°.

(ii) 3-Bromo-2,5-diphenylfuran

To an ice cooled and stirred suspension of sym-dibenzoylbromoethane (11.5 g, 0.03 mol) in freshly distilled acetic anhydride (60 ml) was added conc sulphuric acid (1.5 ml). After 0.5 hr stirring at 0° the clear solution was poured over crushed ice. The resulting yellow precipitate was filtered, washed with water and dried. Crystallization from ethanol gave 7.26 g (67%) of 3-bromo-2,5-diphenylfuran mp 79-80° (lit[55] mp 82-82.5°).

(iii) 2,5-Diphenyl-3-(9'-hydroxy-9'-fluorenyl)furan (6)

To stirred magnesium turnings (0.15 g, 0.006 mol) and dry ether (20 ml) was added over 0.5 hr a solution of 3-bromo-2,5-diphenylfuran (1.5 g, 0.005 mol) in dry ether (20 ml). A crystal of iodine was added and the stirred suspension was held at 38° for 22 hr. A solution of fluorenone (0.9 g, 0.005 mol) in dry ether (20 ml) was then added dropwise and the mixture was heated under reflux for another hour. The reaction mixture was poured

onto crushed ice-dil sulphuric acid and then extracted with ether. The ethereal extract was washed successively with water, saturated sodium bicarbonate, dried ($MgSO_4$) and evaporated. The residue was chromatographed on silica gel. Elution with benzene-hexane gave nearly pure alcohol 6 (0.34 g, 17%) as a pale yellow solid which was crystallized from hot benzene, mp 163-64°.

Anal. Calcd for $C_{29}H_{20}O_2$: (M.wt. 400): C, 86.97; H, 5.0: Found: C, 87.06; H, 5.1.

IR: ν_{max} (KBr) (cm^{-1}): 3448 (-OH), 1124 (C-O).

NMR: $\delta_{(CDCl_3)}$: 7.0 (s, 3 furyl proton) and 7.4 (m, aromatic protons).

UV: λ_{max} (EtOH): 215, 231, 238 and 287 nm.

TLC: Single spot (R_f: 0.73, (benzene:ethylacetate, 50:50)).

(iv) Synthesis of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (2)

A solution of 2,5-diphenyl-3-(9'-hydroxy-9'-fluorenyl)-furan (6) (0.075 g,0.0002 mol) in methanolic hydrogen chloride (7-8 ml) was stored overnight. The first crop of furan 2 (0.042 g, mp 118-119°) was collected. The filtrate was poured into cold water (100 ml) and the yellow solid filtered to yield additional 2, mp 116-117°. The crude products were combined and crystallized from methanol to give pure furan 2 (0.068 g, 88%) mp 122-23°.

This material was identical (analysis, tlc, mixed mp, ir and nmr) with the compound obtained from trans-2,3-dibenzoyl-

spiro(cyclopropane-1,9'-fluorene) (1) and methanolic potassium hydroxide/hydrogen chloride.

Reduction of trans-2,3-Dibenzoylspiro(cyclopropane-1,9'-fluorene) (1) with Zinc-Acetic acid-Hydrochloric acid: Isolation of 1,2-dibenzoyl-1-(9'-fluorenyl)ethane (7)

A stirred suspension of the spiro compound 1 (0.25 g, 0.0006 mol) and zinc dust (0.25 g, 0.0035 mol) in acetic acid (3 ml) was kept at 75-80° for 0.5 hr. Concentrated hydrochloric acid (3 ml) was added in one lot and heating was continued for additional hour. The yellow mixture was decanted and diluted with saturated sodium chloride solution (15 ml). The resulting mixture and the zinc residue was extracted with ether. The ether extracts were washed with aqueous sodium bicarbonate, saturated sodium chloride solution, dried ($MgSO_4$) and evaporated. The crude product on crystallization from benzene gave 7 (0.099 g, 39.4%), mp 212-213° (lit[1] mp 209°).

Anal. Calcd for $C_{29}H_{22}O_2$ (M. wt. 402): C, 86.56; H, 5.47. Found: C, 86.64; H, 5.50.

IR: ν_{max} (KBr) (cm^{-1}): 1664 (-C=O).

NMR: $\delta_{(CDCl_3)}$: 2.1 (d of d, J_{AB}= 18, J_{AC}= 3, A), 3.38 (d of d, J_{AB}= 18, J_{BC}= 10, B), 4.45 (d, J_{CD}= 3, D) and 5.1 (d of t, J_{BC}= 10, J_{AC}= 3, J_{DC}= 3, C), 7.4 (m, aromatic protons).

MS: m/e-402.

TLC: Single spot (R_f: 0.75 (benzene:ethylacetate, 50:50)).

Reduction of 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (2) with Zinc-Acetic acid-Hydrochloric acid; Isolation of 2,5-Diphenyl-3-(9'-fluorenyl)furan (8)

A stirred suspension of the methoxyfuran 2 (0.26 g, 0.0006 mol) and zinc dust (0.25 g, 0.0035 mol) in acetic acid (3.5 ml) was kept at 75-80° for 0.5 hr. Conc hydrochloric acid (3 ml) was added in one lot and heating was continued for an additional hour. The red mixture was decanted, diluted with water and extracted with ether. The ether extracts were washed successively with aqueous sodium bicarbonate, sodium chloride solution, dried ($MgSO_4$) and evaporated. The residue was crystallized from benzene to give white crystals of 2.5-diphenyl-3-(9'-fluorenyl)-furan 8 (0.048 g, 20%), mp 158-59°.

Anal. Calcd for $C_{29}H_{20}O$ (M.wt. 384): C, 90.62; H, 5.21. Found: C, 90.82; H, 5.55.

IR: ν_{max} (KBr) (cm^{-1}): did not show the strong C-OCH_3 (1064) absorption present in 2.

NMR: $\delta_{(CDCl_3)}$: 5.5 (s, 9'-fluorenyl proton), 6.10 (s, furan H), 7.4 (m, aromatic 18 protons).

TLC: Single spot (R_f: 0.69 (benzene)).

Reduction of 1,2-Dibenzoyl-1-(9'-methoxy-9'-fluorenyl)ethylene (3) with Zinc-Acetic acid-Hydrochloric acid; Attempted Isolation of 1,2-Dibenzoyl-1-(9'-fluorenyl)ethane (7)

A mixture of 3 (0.065 g, 0.00015 mol) and zinc dust (0.13 g, 0.0018 mol) in acetic acid (0.5 ml) was heated for

0.5 hr under reflux. Conc hydrochloric acid (3 ml) was added in one lot and after additional 1 hr reflux the red reaction mixture was diluted with aqueous sodium chloride and extracted with ether. The ether extract was washed successively with water, sodium bicarbonate, sodium chloride solution and dried ($MgSO_4$). Evaporation of solvent gave 0.017 g of a carbonyl compound (IR) (C, 57.69; H, 3.60) mp 150-51° which was entirely different from the expected compound.

Reaction of trans-2,3-Dibenzoylspiro(cyclopropane-1,9'-fluorene) (1) with Methanolic Potassium Hydroxide followed by Saturation with Hydrogen Chloride at 0°; Isolation of 1,2-Dibenzoyl(1-fluorenylidine)ethane (9)

To a suspension of 1 (1.0 g, 0.0025 mol) in absolute methanol (25 ml) was added 30% methanolic potassium hydroxide (5 ml) and the mixture was refluxed for 0.5 hr. The blood red solution was filtered, cooled in ice and treated with dry hydrogen chloride until the precipitation of the yellow 9 was complete. The reaction mixture was filtered, washed free of acid and salt, dried and the resulting crude product (0.4 g, mp 195-96°) was crystallized from benzene to give pure 9, (0.382 g, 38.2%), mp 198°.

Anal. Calcd for $C_{29}H_{20}O_2$ (M.wt. 400): C, 86.97; H, 5.04. Found: C, 86.84; H, 5.29.

IR: ν_{max} (KBr) (cm^{-1}): 1692, 1661 (-C=O).

NMR: $\delta_{(CDCl_3)}$: 4.81 (s, methylene protons), 7.4 (m, aromatic protons).

TLC: Single spot (R_f: 0.75 (benzene:ethylacetate(50:50)).

Reaction of 1,2-Dibenzoyl-(1-fluorenylidine)ethane (9) with Hydrazine Hydrate; Isolation of 3,6-Diphenyl-4-(9'-fluorenyl)-pyridazine (11): (Inner azine of 9)

To a stirred solution of 9 (0.040 g, 0.0001 mol) in ethanol:benzene (3 ml, 1:1) was added 2 drops of 85% hydrazine hydrate and the mixture was refluxed under stirring for 7.5 hr. The solvents were removed in vacuo and the crude pale yellow compound was crystallized from benzene to give 3,6-diphenyl-4-(9'-fluorenyl)pyridazine 11 (0.038 g, 96%) mp 238° (lit[1] mp 235°).

Anal. Calcd for $C_{29}H_{20}N_2$ (M.wt. 396): C, 87.8; H, 5.0; N, 7.2. Found: C, 87.58; H, 4.83; N, 7.14.

NMR: $\delta_{(CDCl_3)}$: 5.45 (s, 9'-fluorenyl H), 7.4 (m, aromatic protons).

TLC: Single spot (R_f: 0.36 (benzene)).

Reduction of 1,2-Dibenzoyl-(1-fluorenylidine)ethane (9) with Zinc - Acetic acid-Hydrochloric acid; Isolation of 1,2-Dibenzoyl-1-(9'-fluorenyl)ethane (7)

A mixture of 9 (0.125 g, 0.0003 mol) and zinc powder (0.25 g, 0.0035 mol) in acetic acid (1 ml) was heated for 0.5 hr under reflux. Conc hydrochloric acid (5 ml) was added in one lot and after additional one hour reflux the reaction mixture was cooled and diluted with water. The mixture was extracted with ether and the ethereal extract was washed successively with water, sodium bicarbonate solution, sodium chloride solution and dried ($MgSO_4$). Evaporation of solvent gave the crude product which was crystallized from benzene to give 7 (0.025 g, 20%),

mp 213-214°.

This product was identical (mixed mp, tlc, ir) to that obtained from 1 zinc-acetic acid-hydrochloric acid.

Transformation of 1,2-Dibenzoyl-(1-fluorenylidine)ethane (9) to 2,5-Diphenyl-3-(9'-methoxy-9'-fluorenyl)furan (2)

A suspension of 9 (0.075 g, 0.00018 mol) in absolute methanol (8 ml) was refluxed for 0.25 hr. The hot suspension was saturated with dry hydrogen chloride. The mixture became clear in 2 min. After 0.1 hr excess methanol was removed under reduced pressure and the residue was cooled. The yellow crystals were collected and crystallized from hot methanol to give pure 2, mp 122-23° (0.030 g, 30.8%).

The compound was identical (tlc, mixed mp, ir) to that prepared from 1.

Attempted preparation of (2) from (9) via common intermediate (4) with Methoxide

To a suspension of 9 (0.020 g, 0.00005 mol) in absolute methanol (2 ml) was added 0.5 ml of 30% methanolic potassium hydroxide and the resulting blood red mixture was refluxed for 0.5 hr. The suspension was filtered and dry hydrogen chloride was passed through the hot filtrate until it turned yellow. The reaction mixture on tlc showed major spot corresponding to the methoxy furan 2 along with two other spots.

Attempted Cyclization of (7) to the Furan (8)

To a stirred solution of 1,2-dibenzoyl-1-(9'-fluorenyl)-ethane 7 (0.028 g, 0.00005 mol) in methanol (2-3 ml) was added saturated methanolic hydrogen chloride solution (3 ml) and stirring was continued overnight. Solvents were evaporated. TLC showed no reaction.

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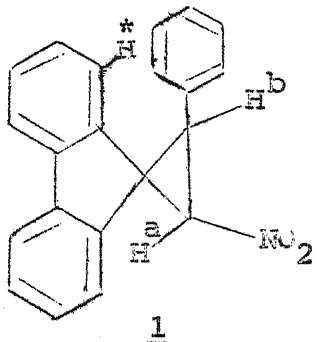
APPENDIX

RESULTS AND DISCUSSION

In the course of routine characterization of spironitrocyclopropanes (Chapter II), the NMR of β-nitrostyrene adduct 1 showed unexpectedly, the presence of a doublet (J = 8 Hz) at 6.15 ppm. Since the cyclopropane protons were readily accounted



1

on basis of doublets (J = 6 Hz) at 5.4 and 4.7 ppm, the 6.15 ppm doublet was concluded to be due to proton H^*, significantly shielded by the phenyl ring. The literature abounds with examples and discussions of shielding of protons by aromatic rings.[1] However, the observed shielding amounting to nearly -1.2 ppm is of significant magnitude and because of lack of information pertaining to the NMR of spirocyclopropanes related to 1, it was considered necessary to examine the spectra of such

compounds. It was hoped that such an examination would not only confirm the assignment for 1 but also provide information about the preferred alignment of the phenyl ring with respect to the remaining rigid part.[2]

The spirocyclopropanes 1-6 were prepared by reaction of the appropriate olefinic functions with 9-diazofluorene. In Table I is presented the chemical shift of this shielded aromatic proton H^* (wherever present) as well as that of the cyclopropyl protons in ppm. The bulk of the aromatic protons appear in all these cases as a complex multiplet centred around 7.3 ppm.

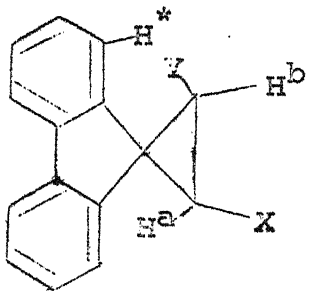
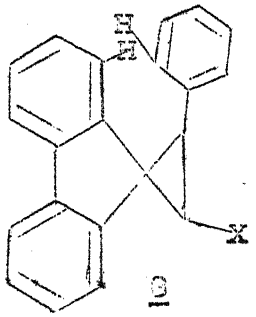


Table I

No.	X	Y	H^*	H^a	H^b
1.	NO_2	Ph	6.15	5.42	4.68
2.	NO_2	H	-	4.8	-
3.	$COOC_2H_5$	Ph	6.15	4.15	3.2
4.	$COCH_3$	Ph	6.2	4.2	3.4
5.	COC_6H_5	Ph	6.3	4.4	4.0
6.	COC_6H_5	COC_6H_5	-	4.5	4.5

Proton H* always appeared principally as a doublet with J = 6-8 Hz and integrating exactly for one proton. The NMR spectra of compounds 1-6 are presented in the following section. A cursory examination of Table I shows that H* appears only when Y = Ph, thus supporting the initial assignment for 1. Molecular models readily explains the shielding of H*. Free rotation of the phenyl ring with respect to the remaining rigid frame work is possible. However, the conformation that is most favoured (7) as well as the one least favoured (8) can be easily identified on basis of non-bonded interactions. In the unfavourable 8, the interaction of H* with C-H of the phenyl ring is maximum.



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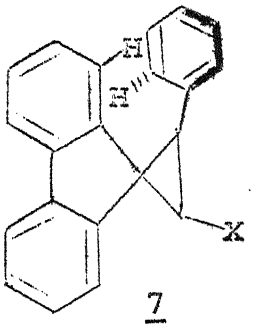
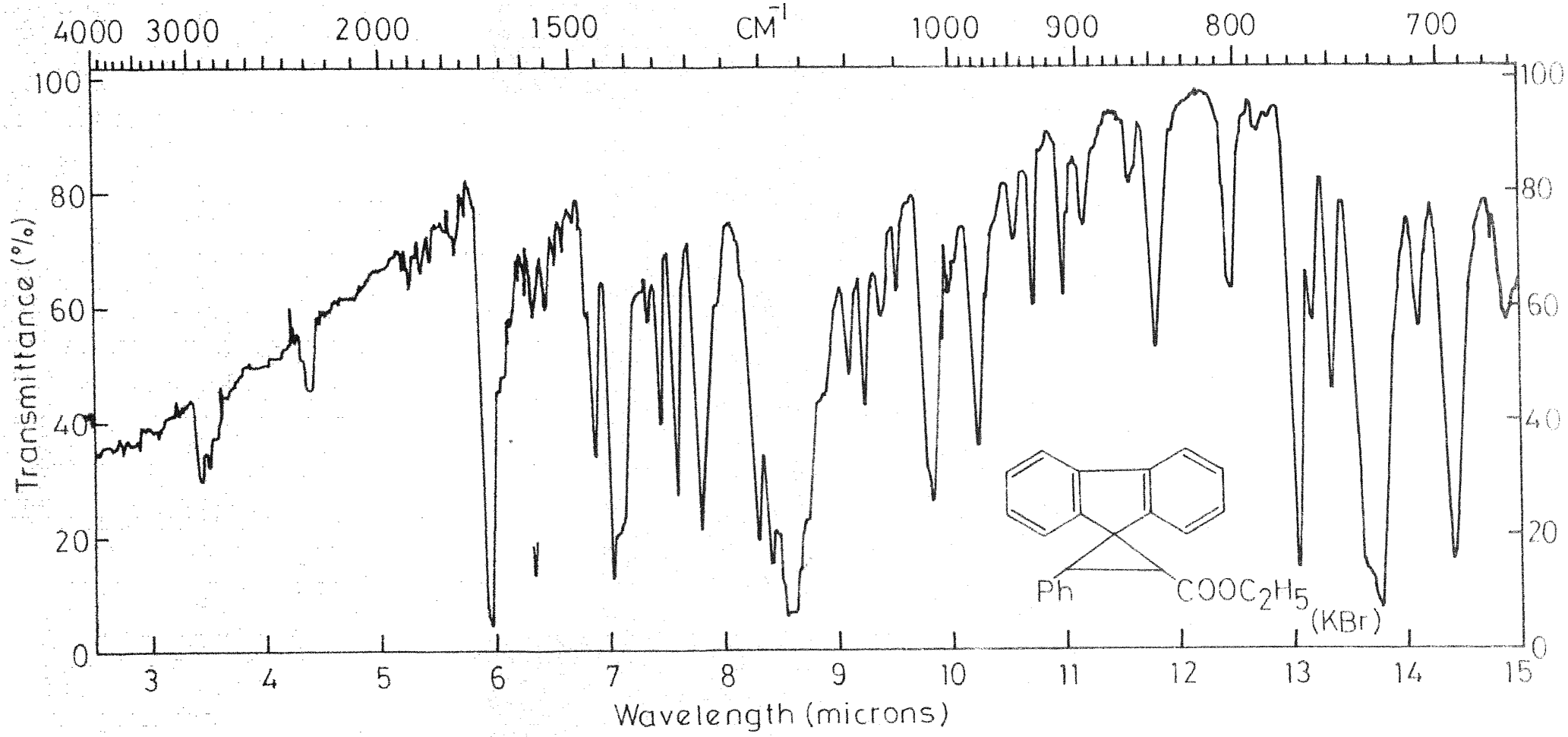


7

The theoretical shielding of H* on basis of the favoured conformation 7 can be calculated using the Johnson-Bovey tables.[3] For this conformation where z = 2 and p = 0.8 the expected shielding is -1.55 ppm and in view of the approximations inherent in Johnson-Bovey calculations as well as those present in the consideration of the Dreiding model as representative of 1-6, the agreement with the observed value, namely -1.2 ppm is quite good and reflect the importance of the preferred conformation for spiro systems represented by 1-6.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80
60
40
20
0
Transmittance (%)
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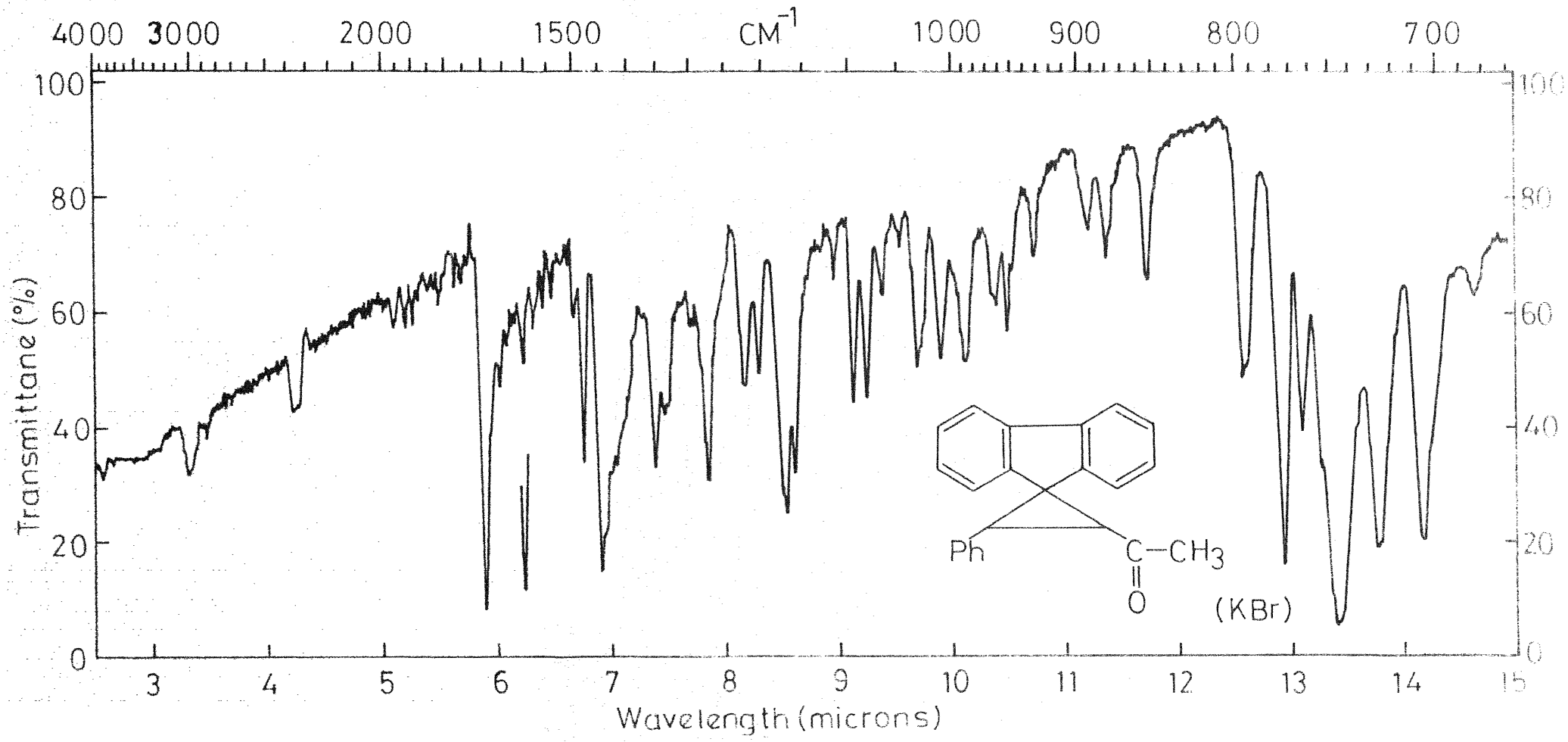
Wavelength (microns)
Ph
COOC2H5
(KBr)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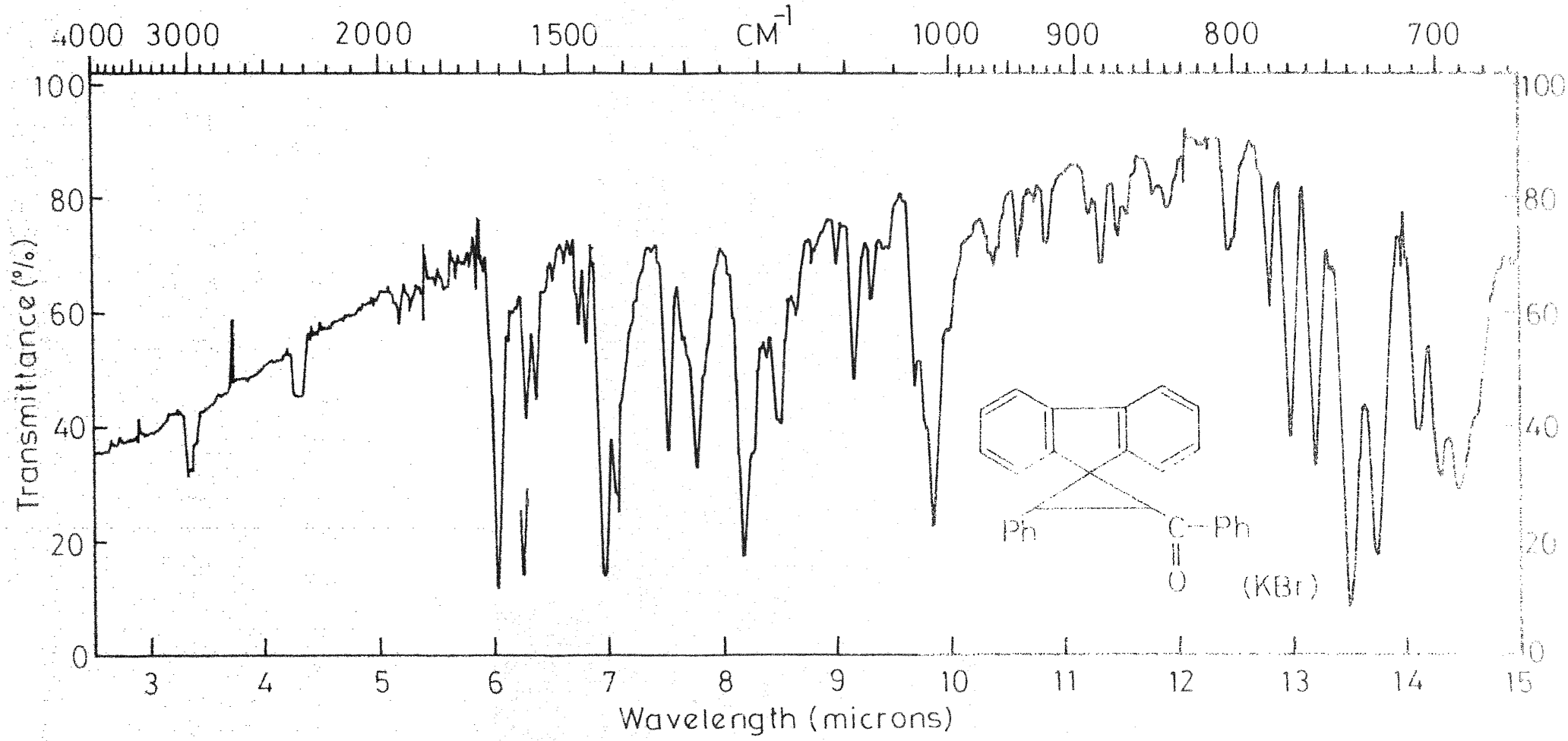
14
15
Wavelength (microns)
Ph
C—CH3
O
(KBr)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Wavelength (microns)
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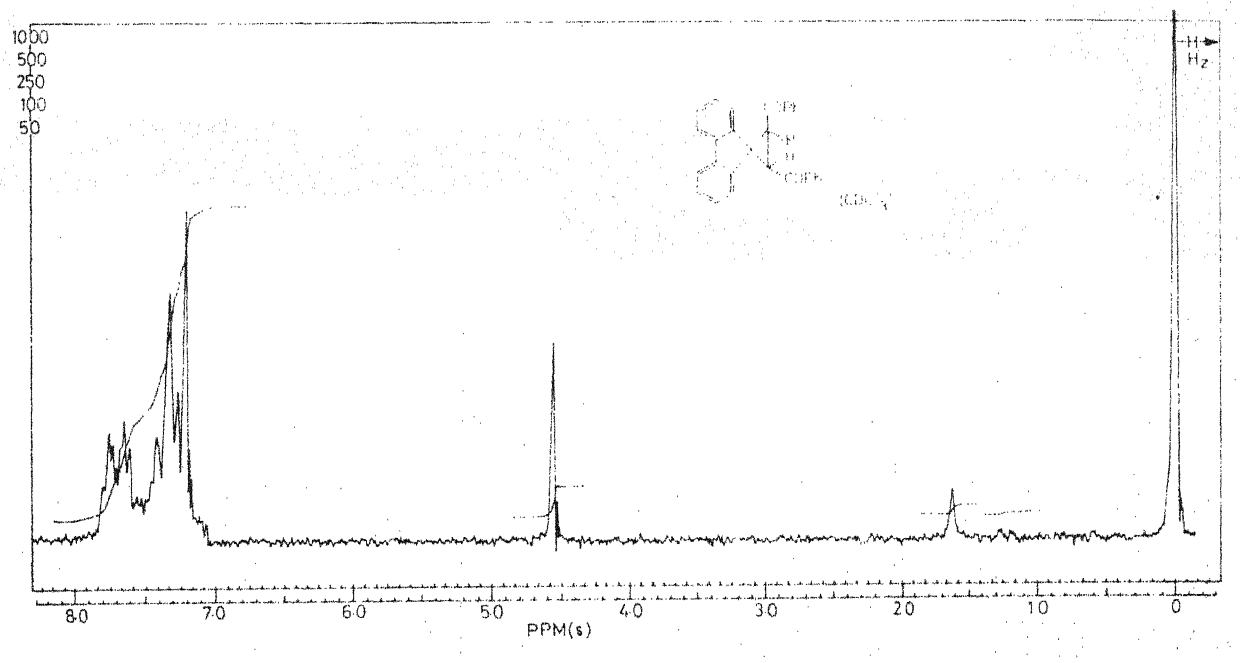
C—Ph
O
(KBr)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Hz
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3.0
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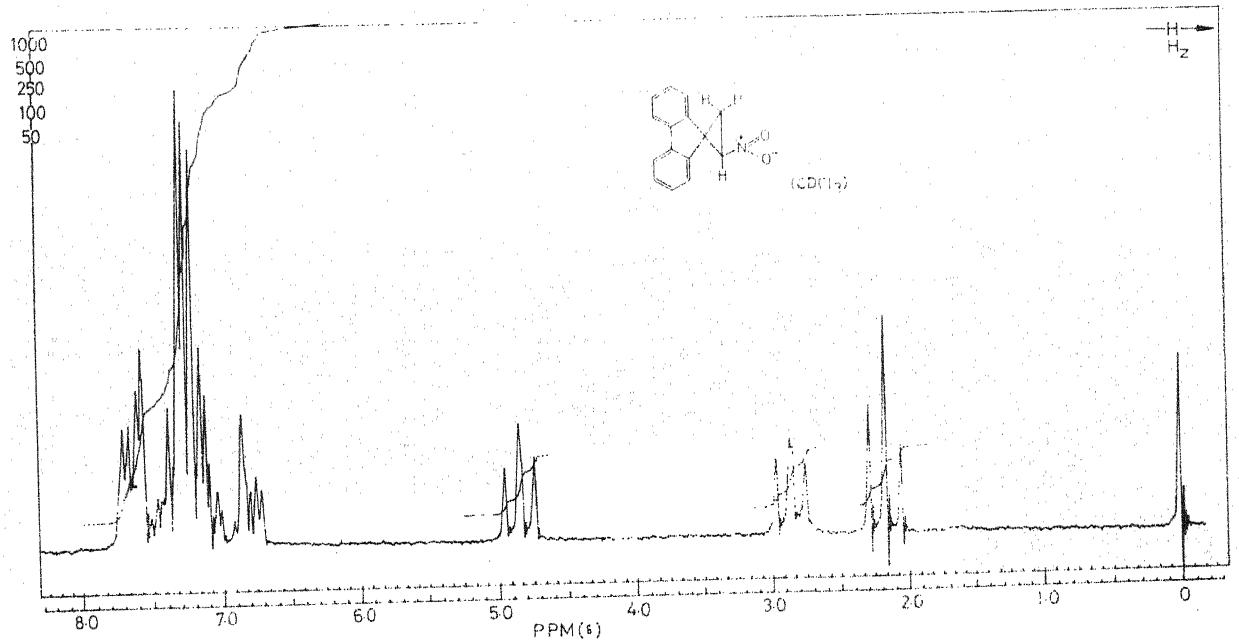
1.0
0
PPM(s)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50
—H—
Hz
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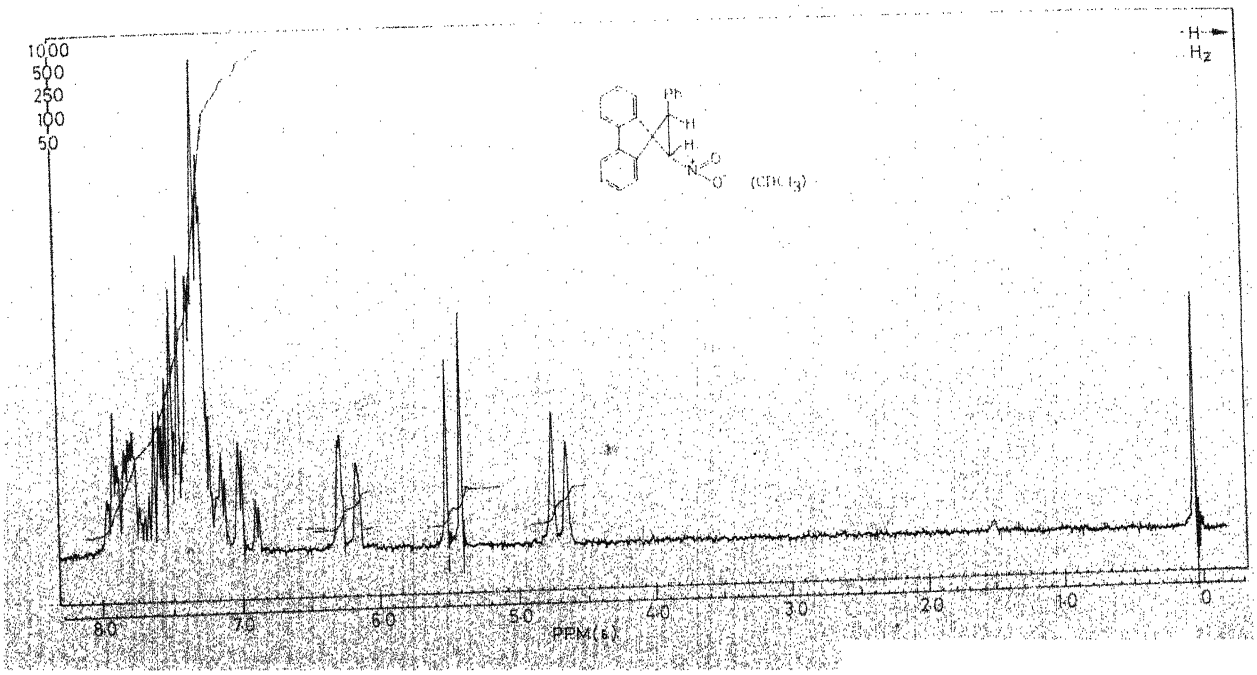
3·0
2·0
1·0
0
PPM(δ)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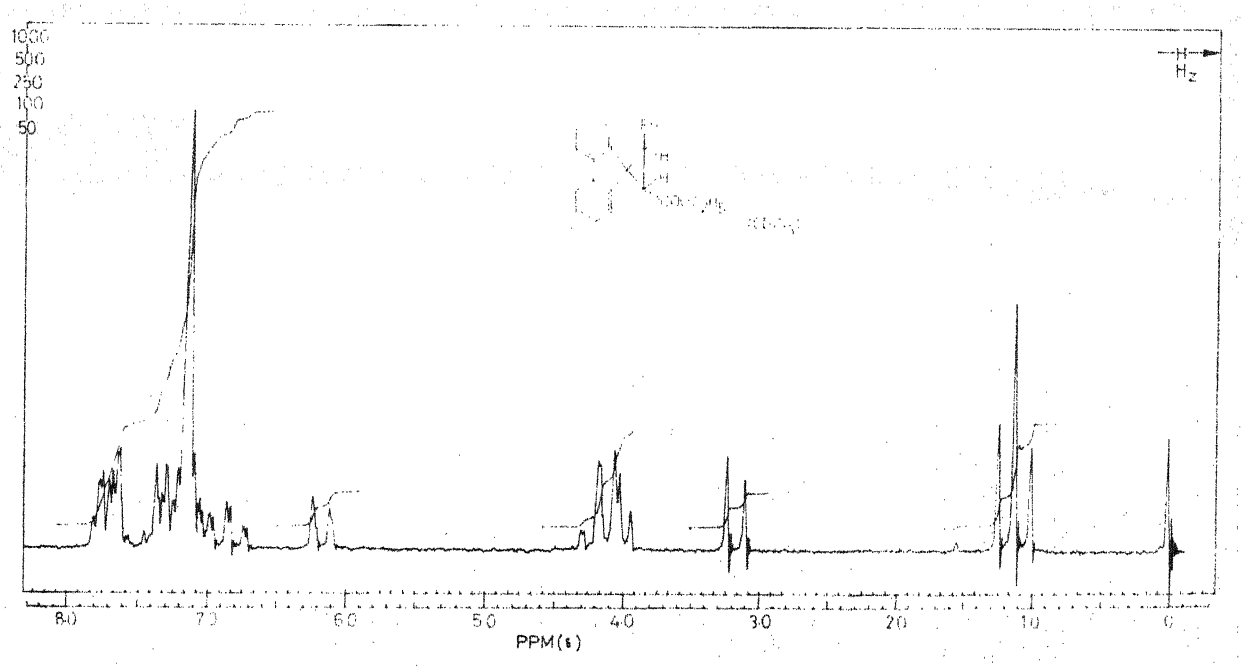
PPM(δ)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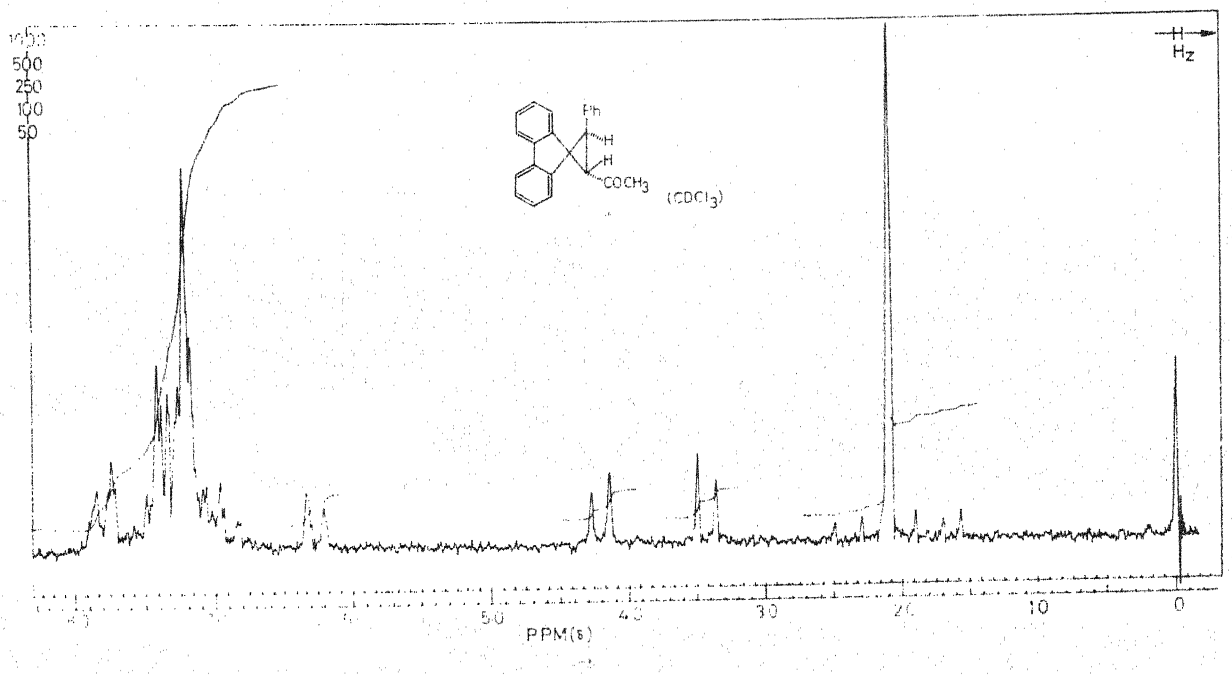
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H
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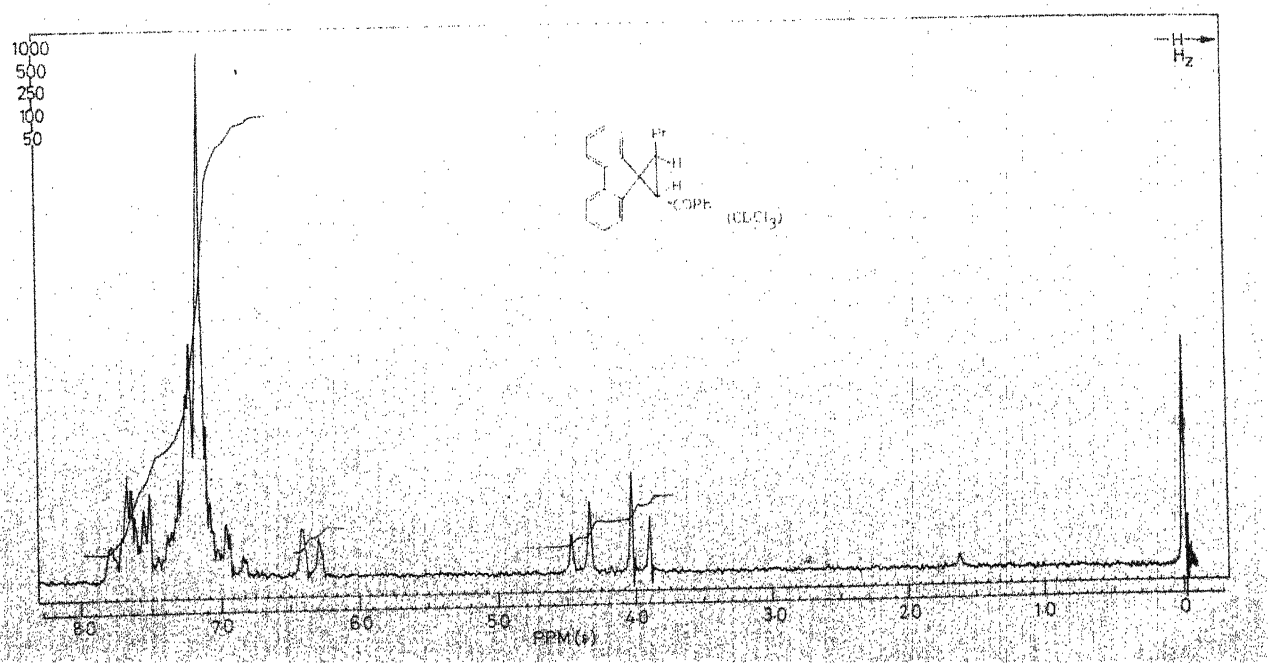
PPM(δ)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PPM(δ)

EXPERIMENTAL

All melting points are uncorrected and were taken on a Fischer-Johns melting point apparatus. Infrared spectra were taken on a Perkin-Elmer - 137 Infracord spectrometer. NMR spectra were determined on Varian A-60D spectrometer, using TMS as an internal standard.

The preparation of 1 and 2 are described in Section II.E and compound 6 in Section III.E.

Reaction of 9-Diazofluorene with Ethylcinnamate: Isolation of 2-Phenyl-3-carbethoxyspiro(cyclopropane-1,9'-fluorene) (3)[4] (trans):

A solution of 9-diazofluorene (2 g, 0.01 mol) and ethylcinnamate (1.83 g, ~ 0.01 mol) in dry ether (30 ml) was allowed to stand at room temperature for three weeks. The crude product, that separated gradually, on repeated crystallization from 95% alcohol gave 1.22 g (34%) of 3, mp 115-116 (lit.[4] 116°).

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.70; H, 5.38. Found: C, 84.42; H, 5.81.

IR: ν_{max} (KBr) (cm^{-1}): 1704 (-C=O), 1176, 1027 and 772.

NMR: $\delta_{(CDCl_3)}$: 1.1 (t, $-CH_3$), 3.2 (d, J = 8 Hz; -CH-Ph), 4.15 (m, $-OCH_2$ and $-CH-COOC_2H_5$ protons), 6.15 (d, J = 8 Hz, -H*) and 7.4 (m, aromatic protons).

TLC: Single spot R_f: 0.69 (Benzene:Ethylacetate, 50:50).

Preparation of 2-Phenyl-3-acetylspiro(cyclopropane-1,9'-fluorene) (4) (trans)

(i) Benzalacetone[5]: To a well stirred mixture of pure benzaldehyde (10.6 g, 0.1 mol) and analar acetone (15.9 g, 0.27 mol) was added cautiously 10% sodium hydroxide (2.5 ml) over a period of 0.5 hr. The mixture was left stirred at room temperature for further 2 hr, made acidic by addition of dil. hydrochloric acid (3N, 10-12 ml). The reaction mixture was extracted with benzene (10 ml). The organic layer washed with water, dried ($MgSO_4$) and evaporated and the residue distilled at 122-130°/8 mm. The distillate solidified on standing to a crystalline mass (10.75 g). The crude solid was crystallized from petroleum ether (bp 60-66°) to give 10.25 g (70%) of pure benzalacetone.

IR: ν_{max}(neat): 1667 (α,β-unsaturated -C=O), 1253, 975 and 749.

(ii) Reaction of 9-diazofluorene with Benzalacetone: Isolation of 4: A solution of 9-diazofluorene (1.16 g, 0.006 mol) and benzal-acetone (0.88 g, 0.006 mol) in dry benzene (10 ml) was left aside at room temperature for two weeks. Addition of petroleum ether (bp 60-66°, 15 ml) precipitated a colourless crystalline material. The crude compound was crystallized from benzene to give 0.735 g (40%) of 4, mp 226-227°.

Anal. Calcd for $C_{23}H_{18}O$: C, 89.03; H, 5.80. Found: C, 89.23; H, 5.86.

IR: ν_{max} (KBr) (cm^{-1}): 1695 (-C=O), 1447, 1171 and 774.

NMR: $\delta_{(CDCl_3)}$: 2.08 (s, $-CH_3$), 3.4 (d, J = 8 Hz; -CH-Ph), 4.2 (d, J = 7 Hz; -CH-Ac), 6.2 (d, J = 7 Hz; H*) and 7.35 (m, aromatic protons).

TLC: Single spot R_f: 0.68 (Benzene:Ethylacetate, 50:50).

Preparation of 2-Phenyl-3-benzoylspiro(cyclopropane-1,9'-fluorene) (5)[7] (trans)

(i) Benzalacetophenone[6]: To an ice-cooled stirred solution of sodium hydroxide (11 g, 0.275 mol, 100 ml) and 95% ethanol (50 g, 61 ml) was added dropwise distilled acetophenone (26 g, 0.216 mol) followed by benzaldehyde (23 g, 0.217 mol) over a period of 0.5 hr. The reaction mixture was left in the ice-chest overnight, the solid filtered, washed with ice-cooled ethanol (10 ml) and dried. Crystallization from 95% ethanol gave 36 g (73%) of pure benzalacetophenone, mp 56-57° (lit.[6] 56-57°).

I.R: ν_{max} (KBr) (cm^{-1}): 1667 (α,β-unsaturated -C=O), 1613, 1337, 1220, 1020 and 755.

(ii) Reaction of 9-Diazofluorene with Benzalacetophenone: Isolation of 5:[7] A solution of 9-diazofluorene (1.338 g, 0.007 mol) and benzalacetophenone (1.45 g, 0.007 mol) in dry benzene (15 ml) was left aside at room temperature for three weeks. The resulting solution was treated with petroleum ether (bp 60-66°, 10 ml) and the solid obtained was crystallized from benzene:petroleum ether (50:50) to give 1.892 g (75%) of 5,

mp 187-188° (lit.[7] 186°).

Anal. Calcd for $C_{28}H_{20}O$: C, 90.32; H, 5.37. Found: C, 90.14; H, 5.24.

IR: ν_{max}(KBr) (cm^{-1}): 1664 (-C=O), 1433, 1220 and 1014.

NMR: $\delta_{(CDCl_3)}$: 4.0 (d, J = 8 Hz; -CH-Ph), 4.4 (d, J=8 Hz; -CH-Bz), 6.3 (d, J = 8 Hz, H*), and 7.4 (m, aromatic protons).

TLC: Single spot R_f: 0.72 (Benzene:Ethylacetate,50:50).

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VITAE

Born on February 12, 1945, in Baramba, Cuttack district (Orissa State), Chandra Sekhar Panda passed his H.S.C. Examination, conducted by Board of Secondary Education, Orissa, from M.S. High School, Baramba in 1960. Later he joined Ravenshaw College, Cuttack and took his Bachelor's degree in Hons. in Chemistry with distinction from Utkal University in 1964 standing Ist in Ist Class in the University. In 1966 he got his Masters degree in Chemistry with specialization in Organic discipline. During 1966-67 he served as a Lecturer in Chemistry at G.M. College, Sambalpur for a little less than a year and joined the Ph.D. Programme in Chemistry at the Indian Institute of Technology, Kanpur, in July 1967. Presently he is working as a Senior Research Assistant in the same department.

He is happily married and blessed with a son with whom he spends his spare time besides chemistry.